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Offices—Aldine House, Bedford Street, Strand, London, W.C. 2.

Telegrams: Instpetech, Westrand, London.
Telephone: Gerrard 6817.

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THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

NOTICES.

The Institution as a body is not responsible for the statements of opinion expressed in any of its publications.

Copyright. Authors of papers and articles are requested to transfer their copyright to the Institution for a period of six months from the date of receipt of the paper. Such transfer should be made in writing when the manuscript is forwarded to the Editor.

Editors are permitted to publish abstracts, providing that acknowledgment is made to The Institution of Petroleum Technologists.

Issue of Journal. The Journal is issued in six parts per volume, commencing in February of each year, with occasional extra numbers when necessary. The Title Page, Table of Contents and Index to each volume are published in the first issue of the succeeding volume.

Members whose subscription is not in arrear receive the Journal free of cost, and additional copies are charged at the rate of 7s. 6d. per part, unless otherwise stated. A member whose subscription is not paid by June 30th of the year for which it is due is considered to be in arrear.

Changes of Address. Members are requested to notify any change of address to the Secretary.

Papers and Articles. Members are invited to submit papers to be read at the General Meetings of the Institution, and are specially asked to forward articles for consideration for publication in the Journal. Diagrams, illustrations, etc., should be suitable for direct photographic reproduction.

Authors of papers published in the Journal are entitled to receive 25 free reprints of their contribution. Further copies may be obtained on payment and orders for these should be sent to the Secretary when the manuscript is forwarded to the Editor. The free reprints do not include any discussion which may be published with the paper, but authors may have such discussion included in their reprints on payment of the additional cost.

Galley proofs of the paper to be read at a General Meeting are available at the time of the meeting, but members desirous of receiving such galley proofs in advance should apply to the Secretary.

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Abstracts. Abstracts of the more important articles and patent specifications are published with each issue of the Journal, this supplement being paged independently of the transactions. Members desiring to have the Abstracts printed on one side of the paper only can be supplied with uncorrected galley proofs at a charge of 10s. per annum per copy, payable in advance.

Medals. The Redwood Medal is awarded, at the discretion of the Council, to the person who shall have made the most meritorious contribution to petroleum technology, in the form of a paper or papers published in the Journal of the Institution, during two successive sessions, preference being given to original work and to papers which have been read before the Institution and discussed. The award is not confined to members of the Institution and may be withheld if no contribution is considered to be of sufficient merit.

A medal and a prize of five guineas is awarded annually by the Council to that Student Member of the Institution who shall, in their opinion, have presented the best paper during the session.

Research Fund. The sum of £400 is allocated in each calendar year to the advancement of Research in Petroleum Technology and its basic sciences, and the Council are prepared to receive applications for assistance from this fund.

Applications from persons proposing to engage in research in any university or other teaching institution must be supported by the professor under whom the applicant will be working.

Applications from Associate Members, Students or Associates of the Institution of Petroleum Technologists and non-members, not proposing to engage in research in any university or other teaching institution, must be supported by a Member of the Institution or other responsible person.

Applications from full Members of the Institution do not require a supporter.

Applications for grants from this fund will be considered in June and December of each year and must be received by the Secretary not later than June 1st or December 1st respectively. Application forms may be obtained from the Secretary of the Institution at Aldine House, Bedford Street, London, W.C. 2.

Advertisements. Advertisements are inserted in the Journal, and information as to terms, etc., can be obtained from Mr. Thomas Tofts, 30 Bank Chambers, 329, High Holborn, W.C. 1. (Telephone No. Hol. 4776.)

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Library. The Institution's Library may be consulted between the hours of 11 a.m. and 4 p.m. daily. (Saturdays, 11 a.m. to 1 p.m.)

PERSONAL NOTES OF MEMBERS AND SPECIAL NOTICES.

It is suggested that members send information regarding their movements to the Secretary, for insertion under this heading.

We offer our congratulations to Sir THOMAS H. HOLLAND on his election as President of the British Association.

Mr. J. D. BING has left for Iraq.

Dr. T. O. BOSWORTH left in August for Ecuador and Colombia, and his address for the next few months will be "Santa Elena," Ecuador.

Mr. G. P. CHAPLIN has returned from Panama.

Mr. J. DALGLEISH is in Burma.

Mr. G. DICKINSON is in Sarawak.

Dr. A. ERDELY is now in Budapest.

Lieut. G. C. FLOWER has returned from Egypt.

Mr. O. H. GRIFFITHS is returning from Albania.

Mr. G. HESELDIN has returned from the U.S.A.

Mr. J. H. HUNTER has returned from Burma.

Mr. A. P. LIESER is now in the U.S.A.

Mr. W. H. LOWE is in Spain.

Dr. W. A. MACFADYEN has left for British Somaliland.

Ing. J. MARTYNIK is now in Germany.

Mr. E. C. MASTERSON has left Rumania, and will be in the U.S.A. for a few months.

Mr. J. MCADAM has left for Persia.

Mr. R. S. MCWHINNIE has returned from India.

Mr. H. F. MOON is in Iraq.

Mr. E. L. MOORE is in Trinidad.

Mr. J. M. MUIR has left Mexico and is now in Texas, U.S.A.

Mr. S. O. NEWTON is in Persia.

Engr. Lt.-Commander G. A. O'NEILL has returned to Las Palmas, Canary Islands.

Mr. R. M. S. OWEN has returned from Venezuela.

Mr. G. E. PONSONBY has returned from California, U.S.A.

Mr. A. E. SOUTHERN is returning to Burma.

Mr. L. F. STOCKDALE is in South Africa.

Mr. A. F. STRICKLAND is home from Trinidad.

Mr. G. F. VAN SENDEN has left Holland and is again in the U.S.A.

Mr. J. L. WELLS is now in India.

Mr. J. H. M. YOUNG has returned from his visit to Australia, Far East and North America.

The Secretary will be glad to receive information as to the whereabouts of the following members:—J. M. BAILEY, J. C. FORTUNE, C. O. GRAHAM, D. H. GWINNER, L. B. HOLLOWAY, K. C. JOHNSON, I. C. LOW, A. F. C. PARKER, L. R. PHILLIPS, J. K. WALTON, W. WALLACE WATT and S. S. WEBB-BOWEN.

The suggestion has been made that complete bound sets of the Journal should be available for sale to members of the Institution. Any member wishing to avail himself of this opportunity should communicate with the Secretary.

STANDARD METHODS OF TESTING PETROLEUM AND ITS PRODUCTS.

In view of the proposed publication during the coming year of a second edition of "Standard Methods of Testing Petroleum and Its Products," it has been decided that the remaining copies of the first edition shall be made available at 3s. per copy on and after January 1, 1928.

RULES FOR THE LENDING LIBRARY OF THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

Members of the Institution may borrow books from the Lending Library subject to the following conditions:

1. Any member resident in the United Kingdom or the Irish Free State who has paid his subscription for the current year, shall be entitled to borrow not more than two books at any one time.

2. The period of loan shall not exceed two weeks.

3. The borrower shall sign for each volume loaned and records of all loans shall be kept by the Librarian of the Institution. Books are not transferable.

4. Any loss or damage shall be made good by the borrower and books not returned within two weeks shall be deemed lost.

5. Suggestions for the acquisition of new books shall be brought to the notice of the Librarian.

6. The postage on books sent to borrowers shall be paid by the Institution and the return postage shall be paid by the borrowers.

SAFETY LAMPS.

Inquiries have been made from time to time in regard to portable lamps for use in petroleum spirit stores or in the presence of the vapour of petroleum spirit. The Secretary of State gives notice that any safety lamp, flame or electric, which has been approved by the Secretary for Mines for use in mines is suitable for this purpose, and in addition arrangements have now been made at the Mines Department Testing Station, Sheffield, for the testing of other lamps of special design which may be considered more convenient for the purpose in question. At the same time the Secretary of State desires to draw particular attention to the fact that the continued safety of any lamp depends entirely upon its being maintained in thoroughly good condition.

Any safety lamp which is not maintained in proper condition or has been tampered with ceases in fact to be a "safety" lamp and its use may result in the very accident which it was designed to prevent.

Home Office.
2nd October, 1928.

FUEL CONFERENCE.

The Transactions of the Fuel Conference, recently held at the Imperial Institute, will be published early in the New Year. All the papers read at the Conference, together with the discussions thereon, will be included in three volumes with a separate index volume. Copies may be ordered from the publishers, Percy Lund, Humphries and Co., Ltd., 3, Amen Corner, London, E.C. 4. If ordered before December 31st, 1928, the price will be £10 net, and after that date £12 net.

STANDARD METHODS OF TESTING PETROLEUM AND ITS PRODUCTS.

Report of the Standardization Committee, giving details of Methods of Test for Petroleum and Its Products.

Price: **3s.** net.

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DECENNIAL INDEX, 1914 to 1924.

The complete index to the first ten volumes of the Journal of the Institution contains some 10,000 references to subjects and localities.

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THE PETROLEUM INDUSTRY.

A brief survey of the Technology of Petroleum based upon a Course of Lectures given by Members of the Institution of Petroleum Technologists at the Petroleum Exhibition, Crystal Palace, 1920.

This work will be found of value to students and those desirous of obtaining an elementary knowledge of the Technology of Petroleum.

A few remaining copies for disposal at **2s. 6d.**

REPORT OF THE EMPIRE MOTOR FUELS COMMITTEE.

The complete Report of the Empire Motor Fuels Committee, containing valuable data relating to Fuels for Internal Combustion Engines.

A few copies are still available to members only at **1s.**

All the above to be obtained from the office of the Institution,

ALDINE HOUSE, BEDFORD STREET, STRAND, LONDON, W.C.2.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

TENTH ANNUAL DINNER.

The TENTH ANNUAL DINNER of the Institution of Petroleum Technologists was held at the Connaught Rooms, Great Queen Street, London, on Wednesday, October 3rd, 1928. The President of the Institution, Mr. Alfred C. Adams, presided over a gathering numbering nearly 200 and was supported by Sir Frederick W. Black, K.C.B., Professor J. S. S. Brame, and Mr. Herbert Barringer, Past-Presidents; Dr. A. E. Dunstan, Vice-President and Honorary Editor; Mr. Arthur W. Eastlake, Vice-President and Honorary Secretary; Major Sir R. W. Barnett, M.P., Mr. Ashley Carter, Mr. A. E. Chambers, Mr. C. Dalley, Mr. T. Dewhurst, Mr. James Kewley, Mr. E. Lawson Lomax, Mr. William Sutton, Dr. F. B. Thole, and Mr. A. Beeby Thompson, O.B.E., Members of Council.

Among the distinguished guests present were: Engineer Vice-Admiral R. W. Skelton, C.B., C.B.E., D.S.O. (Engineer-in-Chief, Royal Navy), Air Vice-Marshal Sir J. F. A. Higgins, K.B.E., C.B., D.S.O., A.F.C. (Air Member for Supply and Research), Major T. H. Crozier (H.M. Inspector of Explosives), Mr. W. St. D. Jenkins, C.B., C.B.E. (Director of Naval Contracts), Mr. J. W. L. Oliver, C.B., C.B.E. (Director of Naval Stores), Sir Joseph Petavel, K.B.E. (Director, National Physical Laboratory), Mr. W. J. A. Butterfield (Chairman, London Section, Society of Chemical Industry), Professor Gregory (President, Geological Society), Mr. L. H. Hounsfield (President, Institution of Automobile Engineers), Mr. G. Patchin (Principal, Sir John Cass Technical Institute), and Professor S. J. Truscott (President, Institution of Mining and Metallurgy).

"The King."

The toast of "The King" was proposed by the President and enthusiastically honoured.

The President then said: Gentlemen, I have received a cable from the Persian Branch that reads as follows: "On the occasion of the first Annual Dinner of the Persian Branch the Branch sends good wishes to the parent Institution." I will read you the telegram which has been drafted in reply: "The President and Members assembled at the Annual Dinner much appreciate the good wishes of the members of the Persian Branch and send cordial greetings on the occasion of their first Annual Dinner." (Applause.) I think the occasion of the first Annual Dinner of the Persian

Branch must be quite a special one, and I hope they will have a full muster and an entirely successful evening.

I now have the privilege on behalf of the Council to present the prizes awarded for the best paper read before the Students' Members Section. The Students' Medal and Prize this year goes to Mr. C. B. Roach for his paper on "Air and Gas Production Methods." I have also a special prize to present to Mr. D. A. Howes for his paper on "The Present Method of Determining Constituent Classes of Hydrocarbons in Gasoline." The Committee, in judging the respective merits of the papers competing for the Students' Medal and Prize, had a task of no little difficulty, and they decided to recommend to the Council that a special prize should be awarded to Mr. Howes for his paper.

The prize was presented to Mr. Howes amid applause.

"The Petroleum Industry."

Eng. Vice-Admiral R. W. Skelton, C.B., C.B.E., D.S.O., R.N., said: Mr. President and gentlemen, I fully appreciate the importance of this toast. The importance of the petroleum industry to this country, the dependence on it of so many other industries—power, transport, heat, light, and a host of other subsidiary industries—the extent of its contribution towards the finance of this country, all these things are impressive. But the mention of the dependence of other industries on the petroleum industry brings me to another point—a matter on which perhaps I may be considered to have a little knowledge, namely, the dependence of the fighting forces of this country on the petroleum industry.

I hesitate to mention the fighting forces just at present because, as you know, there is a Fuel Conference assembled in London in which forty-eight nations are joined, and those of you who attended the opening ceremony will remember that the two very distinguished statesmen who made the opening addresses both alluded to the effect of which such meetings may have upon the peace of the world. But my excuse for mentioning the fighting forces is that their primary object also is peace, and so far as the Navy is concerned you are all aware of that phrase in one of the prayers, that the Navy is for the security of those who go to and fro on the sea "on their lawful occasions."

The fuel of the Navy now is almost entirely oil—petroleum—and the Navy is expected to do a great deal with it. The Army is now becoming mechanised and also to a large extent dependent on petroleum, and I think we generally agree that the Air Force is just as much dependent on it as the Navy. The claim of our national fuel has been put forward very strongly in a new form—the form known as pulverised fuel. We must all hope that our

national fuel will have a future afloat, but for very many reasons with which all of you will be familiar, pulverised fuel, so far as warships are concerned, is almost a practical impossibility. That is not the case with the Mercantile Marine, and it is to be hoped most sincerely that our national fuel has a great future as it has had a great past in the Mercantile Marine.

In a peace-time Navy we are allowed a ration in order to perform our daily duties and to keep efficient. The ration which we are allowed runs very nearly, in tons, into seven figures. We are expected to get more out of a ton than we used to do. In that connexion I should like to say that there have been great advances during the last few years. One of H.M. ships of the latest design goes twice as far on a ton of fuel as did a ship of a design of ten or fifteen years ago.

As to the use of petroleum in the Navy and the methods of burning, all this has been evolved within the Navy, and the Navy can justly claim to be pioneers in the use of petroleum fuel at sea. Experiments began about 1900 and have been going on ever since. Shortly before the war, thanks very largely to the foresight and genius of the late Lord Fisher, oil fuel was adopted as the standard fuel of the Navy and has remained so for almost every design of ship built since that date.

While mentioning the dependence of the fighting forces on petroleum, the industry will realise that in its own sphere it is dependent also upon the fighting forces for its existence, and in the last extremity the petroleum industry must depend on the Navy.

So far as I know, no industry has such a record of freedom from social troubles, such a record of progress and appreciation of modern methods, or such a record of appreciation of the value of scientific investigation as the industry which is represented here this evening, and no industry of which I am aware employs so many scientific people, so many technicians, so many practical people of different kinds as does the petroleum industry. These people are employed from first to last, from the exploration necessary for the finding of crude to the scientific investigation of all the many products which come from a material probably of more complicated structure than any substance known.

It is well known and appreciated that the petroleum industry is ever looking forward to meet the demands of its customers, it is ever investigating new methods, and so far as the treatment which it metes out to its employees is concerned it is a perfect model.

I esteem it a great honour to propose this toast, which I couple with the name of Sir Frederick Black, and I ask you to drink it with all enthusiasm.

Sir Frederick W. Black, K.C.B., B.A., in responding to the toast, said : Mr. President and gentlemen,—I should like to begin with a word of personal welcome to Admiral Skelton. We have had his predecessor, Sir Robert Dixon, amongst us on, I think, three or four occasions, and we have listened to him with great delight. Whenever I hear any representative of the Services speak I am reminded of a little incident that occurred to myself when I was in the War Mission in New York some years ago. I had to speak to a great gathering in that city on the needs of the fighting forces in Europe, and having put into my remarks all the " punch " and " pep " of which I was capable, there got up a gentleman, a secretary in the American Government at Washington, who said that it was obvious that Sir Frederick Black had spoken with all the restraint imposed by his official position. I feel that that is so with Admiral Skelton. One thing I may tell you of him personally. Amongst those numerous decorations that he wears is one which, I suspect, he honours as much as any of them—the white medal for having got very near to the South Pole.

Admiral Skelton has spoken to us of the pioneer work in oil fuel in the Navy as far back as 1900, and of the developments which have taken place right up to date, especially during the last fifteen years.

I think it was in 1926 that, speaking at one of these dinners, I ventured to say to you that for the moment there was something like stability as between supply and demand in the petroleum industry, and Mr. Francis Powell agreed. I do not suppose that either of us thought that condition of things would last for very long. In the past the oscillation of the pendulum has always taken place in the petroleum industry. It would not be a live industry unless it did take place. In 1927 there was a great over-production, as you know. In 1928 I see signs of scientific co-operation of different forces in the industry, especially in America, especially between the scientific and technical side and the economic and business side. This has always been the case to a great extent in the petroleum industry, much more perhaps than in coal. Sir Philip Nash, in a letter in the *Daily Telegraph*, states that he had been examining a list of the papers read at the Fuel Conference and he found that the economic considerations were in almost every paper bound up with the scientific and technical considerations. That is the only way in which these problems are going to be solved.

At the Fuel Conference, now being held in London, I believe forty-eight nations are represented, twenty-two of them are amongst the people who are reading papers ; and I believe that

at home they would speak twelve different languages. My mind reverted to the scriptural story of the Tower of Babel when the differences of language are supposed to have originated, and please remember petroleum pitch was used in the building of that tower.

Now as to this looking to a remote posterity three thousand years hence, it may be very interesting, and we may say that just as there were bronze and other metals, or corn, or oil, three or four thousand years ago in Mesopotamia and Egypt, so civilisation will always find the materials with which it wants to work, and will find them in three thousand years' time just as it finds them to-day. The oil industry has got a good many astute practical men in it, and it is the practice of a good oil concern to take much closer surveys of the trend of events. Any concern will, of course, see its way twelve months ahead to balance supply and demand, and longer. Then it will look three years, five years, perhaps even ten years ahead, and will revise its outlook year by year. That is practical business. It is also the merest commonplace to say that Nature and Man, especially when the Man is a petroleum technologist, are a very powerful combination, and that remote posterity can do a bit of looking after itself.

I come now to one point with regard to which there is a special call for co-operation between the economic and the scientific and technical sides. The most hopeful thing, to my mind, in the situation in the oil industry to-day is that far-sighted men in the U.S.A. are finding a solution for this difficulty. Every petroleum technologist knows that the right way to deal with an oil field is to have a considerable area under the control of one concern—a system of "unit operation," as the Americans call it—which is at work in many modern oilfields—under that system the wells are put down according to what the geologist thinks necessary for the draining of the pool underneath. But in many of the American oil fields the thing that governs the putting down of the well is the ownership of the particular surface, which has no relation to the oil underneath. The result is that six times or twelve times as many wells will be put down as are strictly necessary. You technologists are often told that it is you who are responsible for this over-production, that your excellent and efficient methods have resulted in the earlier bringing in of this vast output. You say, in reply, do you not? "That is true, as technologists we can bring in the oil practically as quickly as you want it, and we can also show you how you may drill your well down to a certain depth and hold your hand or by means of control valves you regulate the flow from different wells according to the needs of the market." Is not this the right and proper system instead of letting the oil flow in such abundance so that the oil salesmen rush about and sell oil

anywhere and everywhere to the detriment, perhaps, of coal and other fuels? I believe that America is on the way to finding methods—legitimate and scientific methods—of avoiding this wasteful exploitation. There may come in a little difficulty of imports from South America or elsewhere, but that difficulty no doubt will be overcome, and we may hope to see that in the near future oil and the other fuels will come into a fairer economic competition with one another than we have ever had before. For that reason I regard 1928 with its great Fuel Conference and the new departure I have spoken of in increased "unit operation" as likely to rank as an important year in the development of the fuel industry.

"Our Guests."

Mr. Herbert Barringer, in proposing the toast of "Our Guests," spoke as follows: We are always delighted on these occasions to welcome our friends when they honour us with their presence. I have before me a list of the names of some of the distinguished guests who are with us, I hope you will allow me also to refer to one or two others who are unable to come this evening and have sent us their apologies and regrets. Among these are our friend Mr. Powell, also Sir George Higgins (Chairman of Lloyd's Register) and Sir Hugh Trenchard (Chief of the Air Staff). Among the distinguished guests who are with us we have Vice-Admiral Skelton, who has already spoken, and Air Vice-Marshal Sir J. F. A. Higgins, who deals with a lighter form of fuel. We have also two Naval Directors, Mr. Jenkins (Director of Naval Contracts) and Mr. Oliver (Director of Naval Stores). Upon the efforts of these gentlemen, I am sure, Admiral Skelton very much relies. Then we have Major Crozier (H.M. Inspector of Explosives) and Sir Joseph Petavel (Director of the National Physical Laboratory), to whom we look for the most welcome and important assistance in our experiments. Another visitor is Professor Truscott (President of the Institution of Mining and Metallurgy), and yet again Professor Gregory (the President of the Geological Society). Other visitors include Mr. W. J. A. Butterfield (the Chairman of the London Section of the Society of Chemical Industry), Mr. L. H. Hounsfield (the President of the Institution of Automobile Engineers), and Mr. G. Patchin (the Principal of the Sir John Cass Technical Institute). To all our guests we offer a very hearty welcome, and I call upon you to drink their health, coupling with the toast the name of Eng. Rear-Admiral Roome.

Eng. Rear-Admiral G. W. Roome, C.B.E., R.N.: I have listened with great pleasure to the speeches by Eng. Vice-Admiral Skelton and Sir Frederick Black, but unfortunately these gentlemen

have forestalled me on several points I intended to make myself. I have had a good deal to do with the burning of oil fuel in the Royal Navy and Merchant Marine, and my duties and those of Eng. Vice-Admiral Skelton have been much alike in this respect. I started with the Battleship " Prince George " in 1905 with North country coal and oil fuel burned together and extraordinary good results were obtained with that ship under these conditions, showing that a gaseous fuel could be burned satisfactorily and economically in ordinary cylindrical boilers.

When I left the Navy in 1919 I was employed at once with the Canadian Pacific Steamship Company and we converted several of those vessels to burn oil fuel in place of coal in their boilers : we obtained general economical results at the price at which we could buy the oil, but the reason why oil fuel is preferred is largely on account of the saving in labour.

We employ about one-fourth of the men in the stokeholds when we are dealing with oil as compared with the number we should employ if we were dealing with coal ; the use of oil involves much less general cleaning in large passenger ships, a further saving in labour. The choice of oil fuel therefore has led to a number of firemen and trimmers being out of work and also to some extent to unemployment amongst miners, for the demand for coal is so much less than formerly.

The point I wish to make is this, the use of oil as fuel, whether under boilers or in Diesel engines, has reduced the labour necessary to obtain the power, but it is a question whether, as far as our country is concerned, we ought not to try and burn coal in ships even at the expense of some economy, seeing that the coal is our national asset. Vice-Admiral Skelton has pointed out, and I agree, that so far as the Navy is concerned we must use oil fuel, the great powers required could not be obtained otherwise, but in our Merchant Service coal could do the work, and it appears to me it would be patriotic to do so, as far as possible.

A petroleum technologist, I have gathered from previous speeches, may be a geologist, an engineer, a chemist or a user of petroleum for any purpose, but it is to the chemist we must look for the great need of the moment, which is to produce economically from coal a fuel oil which can be used for the same purposes as imported petroleum is used now ; it would find work for our miners and make use of the fuel we have available at home here in this country.

The burning of coal in powdered form is being carried out now in various directions, but will always have the disadvantage of the handling of coal in bulk, but even so will lead to additional employment, and is a step in the right direction, viz., to make use of the

fuel we have available at home. We must look to the chemist technologist and the petroleum chemist technologist in particular to originate the method first.

On behalf of your Guests I thank you.

"The Institution of Petroleum Technologists and The President."

Air Vice-Marshal Sir J. F. A. Higgins, K.B.E., C.B., D.S.O., A.F.C., in proposing this toast, said: Mr. President and gentlemen, this is the first time I have had the honour of proposing the toast of a learned society, and I think it is very appropriate perhaps that my first experience should be to propose the health of the Petroleum Technologists. I am here, I suppose, as the representative of the Royal Air Force, and between the Royal Air Force and the Institution of which I am a guest to-night there is a very close link. Before the petrol engine came into existence, although many inventors had foretold that flying would be in time practicable, very little had been done. When the petrol engine was invented then flying became a possibility, and as the engine became more efficient the greater became the possibilities of aviation. With the still increasing efficiency of the petrol engine the possibilities of aviation will still further increase.

Admiral Skelton, in addition to many other points, has remarked on the importance of the petroleum industry, and therefore of your Institution, to the Services. The Royal Air Force would be completely paralysed if it were not for petroleum. I think perhaps the Royal Navy would now for a time be paralysed also if petroleum suddenly went out of existence. The Army also in these days of mechanisation is very greatly dependent on petroleum and its properties. It is not only Service developments that are concerned.

May I now turn for one moment to a more parochial side of the question, namely, the aviation side of petroleum. The Royal Air Force is a fairly large customer in your industry. It is not, I imagine, anything like as large a customer as many other bodies, but it is probably a much more troublesome one. And it is quite right that it should be a troublesome customer, because a great deal of the improvement in aviation depends on the improvement in fuel, both as to quality and to other things which perhaps are not exactly concerned with the innate quality of the fuel. First of all, as regards quality. The better the petrol you give us the more efficient are the engines we make for the petrol, and the more we demand a better petrol for the engines we produce the more advantageous it is for you if you will regard the matter from an impersonal standpoint, because it makes you strive to put forward your utmost efforts. In that way the result is to increase the efficiency of the

whole of your industry as well as the efficiency of our aeroplanes.

I look on the Institution of Petroleum Technologists as a clearing-house for all the efforts in this direction. One speaker asked what was a petroleum technologist. Well, I suppose a petroleum technologist is a geologist, a chemist, a civil engineer, a mechanical engineer, and a mining engineer. You will know better than I do whether such an extraordinary symposium of all the virtues exists; perhaps it exists in a committee and not in one individual. At any rate, all these experts are necessary in order to exploit the use of petroleum to its utmost extent.

In addition to quality, so far as we are concerned—and I hope you will not think I am dwelling too much on our own particular needs—we also want uniformity. It is a very distressing thing to make an engine which will work extremely well on a fuel which you may get in England and then send it out to another country 3,000 or perhaps 10,000 miles away and find that it will not work at all on the fuel obtaining there. This is not only distressing, but the results very often are almost fatal, and therefore we appeal to your Institution to try and improve both uniformity and quality.

There is another point on which we are extremely interested—a point alluded to by another speaker this evening. This is the weight of the fuel. The weight of the fuel is absolutely one of the first questions so far as aviation is concerned. It is apparent that to get a certain number of miles it is necessary to have a certain amount of fuel; if the efficiency of the fuel or of the engine can be increased so that twice the number of miles can be accomplished on the same weight of petrol the efficiency of aviation, both military and civil, is increased twofold. Now there are several ways in which this question can be attacked. The engine experts can attack it in one way, by making engines which will burn heavy oil instead of petrol. This by the nature of things is much more economical, and for the same weight will give a much increased efficiency. At the same time there may be another method of attacking the problem. You may be able to get a light fuel which can produce something approaching the same efficiency as a heavy oil. Both these lines of investigation are of very great interest to aviation both civil and Service. Your Institution is the body to which we look to obtain these results.

I hardly like to touch on another point, namely, the question of home supplies. There is no petroleum in this country, so far as I know, or very little, and I rather gather that the producing of liquid fuel from coal is a matter which is somewhat outside your purview. At the same time, may I say this, that it is very important to Great Britain that she should be able to get fuel from her own resources and it is a question which I think ought to be taken up

and thought about by your Institution—the question of getting fuel oil from coal. Another speaker has alluded to it this evening. In spite of the fact that we hope the Navy will always be able to ensure that our sources of petroleum from abroad will be sufficient to keep us supplied with our essential requirement in the way of oil, yet regard must be paid to this fact, that without fuel every possible activity which now exists in a civilised country is bound to die. Therefore we must look to our own resources for this fuel supply, and I ask you to think about the question of obtaining fuel oil from coal or from our own native resources as well as from petroleum. I hope I have not introduced a topic which is outside the scope of your body. I join with what other guests have said in expressing the honour which we feel at being asked to this dinner, and our sense of the enjoyment of your hospitality. I propose this toast, which I couple with the name of your President, with the heartiest good wishes for the further success of your Institution.

The President (Mr. Alfred C. Adams), in responding to the toast, said: Gentlemen, We are holding our Annual Dinner this year rather earlier than usual, and it may be that on that account we have to be without the company of many of our friends whom we are accustomed to see on these occasions. But the date was purposely fixed in order to secure the attendance of a number of others who very shortly will have to return to the East. They come over to this country for a short time, and we are only too pleased to make arrangements to have their company before they go back.

I desire to thank Sir John Higgins very warmly for the generous terms in which he has proposed the health of the Institution, and I also want to thank our guests for their cordial reception of the toast. It indicates the interest that they take in our activities. It is one of the privileges of the President to reply to the toast of the Institution, and it seems to me that it enables him to gauge by its reception the extent to which we see ourselves as others see us. I am particularly grateful to Sir John Higgins for speaking so kindly of the Institution. I feel sure that we have genuinely tried to deserve the good opinion of our many friends. But he has also indicated to us that he is not entirely satisfied in some respects, and he has exhorted us in this Institution to see if we cannot do something to remedy the shortcomings about which he has spoken so frankly. Apart from that, which is a matter that we must consider, his remarks will come as a great encouragement to the petroleum technologist and will act as a stimulus to his labours in many fields. The long sojourn of Sir John Higgins in the neighbourhood of what is thought to be one of the most productive oilfields in the world entitles us to salute Sir John himself

as a technologist and as one who is especially qualified to speak to us on the subject of this toast.

In this Institution we do recognise that the uses of petroleum are universal, and that it has become perhaps the most vital necessity of our civilisation. We all know quite well that the navies, armies, air forces, and merchant navies of the world all depend upon the product which has brought our Institution into existence, and there is every reason to doubt whether civilisation in our lifetime would have progressed to anything like the extent it has done had it not been for petroleum. Not only has petroleum helped us in transport, both for commerce and for pleasure, but it has been a necessity and has proved a friend in very many sciences, including medicine. One has only to remember the remarkable strides which electricity has made in our lifetime to realise that without petroleum and its by-products electricity could not have played such an important rôle as it has come to do to-day in our ordinary existence. So far as commercial transport is concerned, petroleum not only propels the vehicle but enters into the preparation of the road on which that vehicle travels. Whatever may be the future in store for petroleum, there is no doubt whatever that it is very much to the fore to-day, and I am optimistic enough to believe that research will still be able to discover new uses to which petroleum can be applied.

As regard the Institution itself, I am entitled to say, I think, that it has progressed on parallel lines with the petroleum industry as a whole. I may perhaps be pardoned if, however modest I personally may feel, I am bold enough to suggest that the rapid progress of the industry in recent years has been due in a great measure to the activities and influence both of this Institution as a corporate body and of its individual members in their own specialised domains. Recognising as we do the advantages of co-operative progress, we have established three branches—in Rumania, in Persia, and in Trinidad. The Rumanian and Persian branches have been established for some time. They number some sixty-five members each, and are very flourishing off-shoots of the parent tree. The Trinidad branch was founded on January 1st of this year, and has developed also into a vigorous and important branch. The establishment of further branches, where useful and practicable, is engaging the attention of the Council.

Our membership is steadily increasing. We have 1,061 members, and there are sixty candidates at present awaiting election. We have enrolled 100 new members this year. Our Students' Section comprises 112 members, and meetings of this section have been held regularly in London and Birmingham throughout the year. The Students' Section per se forecasts the future progress of this

Institution better than anything of which I can think, and we can confidently hope for the success of our Institution so long as we have a strong Students' Section. After all, the students of to-day will be the members of the Institution to-morrow.

As a corporate body our Institution has made itself felt by the fact that it was represented officially by Dr. Dunstan and Mr. Hubbard at the Eighth Congress de Chimie Industrielle, held at Strasburg this year. It is also represented on the World Power Conference now sitting. Your President has the honour of being a member of the Grand Council, and Dr. Dunstan represents the Institution on the British National Committee. The Institution is also represented officially on such important bodies as The American Society for Testing Materials, The Advisory Board of the Department of Oil Engineering and Refining of the University of Birmingham, The British Association for the Advancement of Science, The British Engineering Standards Association, The Fuel Economy Committee, The Imperial Mineral Resources Bureau, and The Mechanical Warfare Board.

No small portion of the service which the Institution renders to its members is carried out by means of the library, the work in which has increased considerably owing to inquiries from all parts of the world. The attendance of members as well as visitors at our library shows a steady increase. A general lending library for members has been established, and while its books may not be numerous as yet, it is replete with the most important publications on petroleum technology, and the number is being continually added to by careful selection. The work of the Standardization Committee is still proceeding. I am afraid I have been somewhat too optimistic in expecting that the revised book on the testing of petroleum and its products would be ready for publication this year. Necessarily the issue of such an important book could not be hurried, but I hope it will be ready in the new year, and when published it will form an up-to-date handbook, the value of which cannot be overestimated.

Sir John Higgins and others have been exchanging opinions as to what is a petroleum technologist. Well, the constituent elements of this Institution consist of geologists, engineers, and chemists, working together on the great problems of petroleum, they form just the right mixture for carrying on the research necessary in so great a subject. So soothing is the benign effect of petroleum that these scientists, in the interests of petroleum technology, in their different branches of work, become perfectly blended in a complete harmony of interests, and in that way the Institution is able to dedicate its full activities to the uses and development and organisation of petroleum.

The Institution is fully alive to the fact that the petroleum industry has now lived for a considerable number of decades, and that the governing features of the industry's progress are supply and demand. Not only does it depend upon the most up-to-date and perfected methods of production, but it has to reckon with the fact that the user of petroleum is getting more and more educated every day. The competition in the markets is keen, and the user must be supplied with an article which will satisfy his requirements, however exacting they may be. That is a confession which I hope will comfort Sir John Higgins when he tells us that he is not entirely satisfied with the products supplied to him. If the producer, refiner, and distributor, utilising all the opportunities that present themselves, are to succeed they must of necessity depend on the oilman of to-day who, in his turn, has to have at his command, in addition to his commercial ability as a salesman, practically the whole of the sciences which go to the making up of the petroleum technologist. We are living in an age when the most accurate technical advice and information is necessary for the trader as well as the producer and refiner, and here comes in not only the service rendered to the industry as a technical body by the publication in the Journal of all the information on the sciences which enter into our work, but also the service of the individual members of the Institution, most of whom are recognised specialists of world-wide reputation in their particular branch of our industry. Through their writings and the publication of the results of their research in the Institution Journal, the utmost help is afforded to the industry as a whole.

In furtherance of its aims of service to the industry, the Institution has provided from its funds research grants and scholarships, and has instituted and distributed medals and prizes to students. One part of our aim is signified by our participation in the deliberations of the World Power Conference. The Institution is, I venture to think, carrying out the principles referred to at the opening of that Conference as to the necessity for the pooling of knowledge in the cause of co-operative progress. I believe that in a large measure the success that has attended the Institution is due to the recognition of this principle by the Council.

I have endeavoured to give you an exterior view of the work of the Institution. Any interior view I can give you cannot be presented in so convincing a manner. I must content myself by saying that a great deal of service is rendered by Dr. A. E. Dunstan, the Honorary Editor, and our thanks are due to him for so successfully editing the Journal and contributing so much to its success and prestige as a publication. I suppose there is no scientist who has contributed more to the cause of petroleum

technology than has Dr. Dunstan. Included in our thanks is Mr. George Sell—our Assistant Editor—who also acts as Secretary of the Standardization Committee. Our Honorary Secretary, Mr. Arthur W. Eastlake, still carries on his labours in the interests of the Institution, and we hope that there will be an improvement in his health so that we can see more of him in our meetings.

To our Secretary, Commander R. E. Stokes-Rees, and his staff we owe our very hearty thanks. Commander Stokes-Rees is assiduous in the work he does for us. I also desire to thank Mr. Ashley Carter for so kindly undertaking the arrangements for this dinner. He does it every year in a very patient and painstaking way, and always carries out the details in a most charming manner.

INSTITUTION OF PETROLEUM TECHNOLOGISTS.

The One Hundred and Thirteenth General Meeting of the Institution of Petroleum Technologists, held at the House of the Royal Society of Arts, on Tuesday, October 9th, 1928, Mr. ALFRED C. ADAMS, President, in the Chair. The following paper was read :—

The Analysis of Cracked Spirits.

The Determination of Aromatic, Olefine, Naphthene and Paraffin Hydrocarbons.

By F. H. GARNER, Ph.D., M.Sc., F.I.C. (Member).

THE importance of cracking to supplement the natural spirit present in crude petroleums is well recognised at the present time, and in view of the anti-pinking qualities of these spirits, in some instances cracked spirits are sold at a premium over straight-run spirits.

Analysis of such spirits has been a matter of considerable difficulty, because there is no satisfactory method of separating olefines from aromatic hydrocarbons.

The question of the relative values of the various types of hydrocarbons—aromatic, olefine, naphthene and paraffin—has aroused considerable interest of late because of the increased power obtainable from the internal combustion engine if the compression ratio can be satisfactorily increased. A survey of the subject has been made by Ricardo, who has tested on his variable compression ratio engine several gasolines, three normal paraffins, three aromatic hydrocarbons and two of the cyclohexane hydrocarbons in fairly pure condition. As a large proportion of the naphthenes in gasolines is undoubtedly composed of cyclopentane hydrocarbons, we have at present no satisfactory value for this group of hydrocarbons. Dr. Edgar has shown that a branched chain octane, 2·2·4-trimethylpentane, possesses anti-knocking qualities of approximately the same order as toluene, whereas normal octane is of a knock-inducing

character. Similar branched chain paraffin hydrocarbons have been found in straight-run gasolines, and it is obvious that further work must be done before any satisfactory value can be ascribed to the paraffin hydrocarbon content of gasolines. It is possible that in one gasoline, normal hydrocarbons may predominate whilst another gasoline may consist almost entirely of branched chain hydrocarbons, but the evidence available points to a general similarity in the composition of all natural gasolines.

If we had a satisfactory method of analysing petroleum spirits for paraffin and naphthene hydrocarbons, then it should be possible definitely to settle this question by determining the Highest Useful Compression Ratio or knocking values for a number of gasolines and ascertaining the H.U.C.R. or knocking values of the paraffin, naphthene and aromatic hydrocarbons from the percentages of these hydrocarbons present. It would be necessary to compare gasolines of similar distillation range, for we already know that, in general, the lower the volatility, the lower the anti-knocking qualities of the fuel. The methods of analysing the gasolines tested by Ricardo are not given, but satisfactory data cannot be deduced as to the relative value of the paraffins and naphthenes from the analytical results given for the various petrols which he investigated, as these gasolines are of very varied distillation range.

A modification of the method of analysis for paraffins and naphthenes (using the aniline point) is described, which is based on experimental figures for pure naphthenes and paraffins, and in this method allowance is made for the variation in the distillation ranges of the petrols examined. The method described is available also for the analysis of the naphthene and paraffin content of straight-run spirits.

Recent work has shown that sulphuric acid does not effect a satisfactory separation of the olefines and aromatic hydrocarbons present in cracked spirit, as in addition to the polymerisation of olefines, condensation of olefines and aromatic hydrocarbons also occurs. A method of analysis has been devised and is described later, which gives results with a fair degree of accuracy—probably ample for the purpose of correlation of analysis and engine tests, whether determined by the Variable Compression Engine or with the aid of the Midgley Bouncing Pin.

It appears probable that branched chain olefines are present in fairly large proportions in cracked spirits as would be expected in view of the fact that the material cracked is composed mainly of branched chain and cyclic hydrocarbons (*i.e.*, gas and lubricating oil fractions contain only small proportions of paraffin wax which is composed of the normal paraffin hydrocarbons).

General Description of Method of Analysis.

The following determinations are carried out in the method of analysis given in the present paper :

(*a*) Olefine and aromatic hydrocarbons are removed simultaneously from the cracked gasoline with the aid of nitric acid, and the aniline point of the remaining spirit is used for the estimation of the percentage of paraffin and naphthene hydrocarbons.

(*b*) The aniline point difference before and after the acid treatment is determined, and also the percentage loss in volume.

(*c*) The iodine number of the original petrol is found.

In order to eliminate as far as possible certain errors in the various measurements, a slightly different method of procedure is adopted with different gasolines for reasons which are discussed later.

Olefine and Aromatic Hydrocarbon Content.—Method No. 1.—*Iodine Number above* 25.—From the difference in aniline points before and after treatment, the *aromatic hydrocarbon equivalent* of the hydrocarbons (olefine and aromatic), removed by the nitric

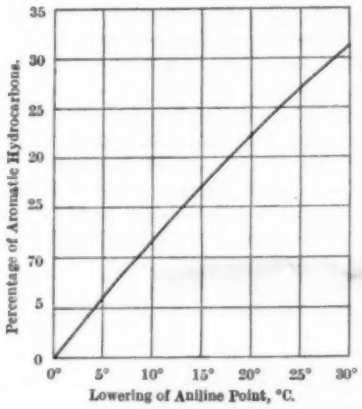

Fig. 1.

acid treatment, is found by reference to the curve, Fig. 1*. The difference between the aromatic hydrocarbon equivalent and the percentage loss of volume is now multiplied by five and then divided by three, giving the olefine content of the original gasoline. The *aromatic hydrocarbon percentage* is the difference between the percentage loss in volume and the olefine percentage determined in this way.

* Tizard and Marshall, *J. Soc. Chem. Ind.*, 1921, **40**, 20r.

METHOD No. 2.—*Iodine Number below* 25.—The olefine content is estimated by dividing the iodine number by the following factors: 2·8 for aviation spirit (mid-point 95° C.), 2·7 for No. 1 spirits (mid-point 105° C.), and 2.6 for all other gasolines.

The aromatic hydrocarbon equivalent is determined as in Method No. 1 from the difference in the aniline points; from this figure is subtracted two-fifths of the olefine content, and the difference is the percentage of aromatic hydrocarbons in the gasoline. In this method there is no necessity for determining the loss in volume during acid treatment.

The usual grades of benzole mixtures come within the limit of 25 iodine number, and it is this type of spirit which tends to give inaccurate results in the determination of loss in volume during acid treatment.

All the results determined in this way are *percentages by weight*, not by volume. With some gasolines, both methods give precisely the same results, but the Method No. 2, in which the olefine content is calculated from the iodine number, if used to determine the olefine content where the iodine number is over 25, often gives erroneous results, as the extent of substitution in the iodine number determination varies according to the type of crude from which the cracked spirit is made.

Thus, the figures for iodine number conversion to olefine content are not always accurate, as the number given for heavy spirits may vary from 2.6 to 2.9 in exceptional instances, and hence this method is limited in general to iodine numbers below 25. Further, where the iodine number is below 4, the gasoline is assumed to be fully saturated, and for low iodine values the following additional conversion factors are suggested :—

Iodine Number.		Olefine Content.
4	..	0·
5	..	0·5
6	..	1·
7	..	1·5
8	..	2·
9	..	2·5
10	..	3·
11	..	3·5
12	..	4·
13	..	4·5
14	..	5·
15	..	5·5

Paraffin and Naphthene Content.—The aniline point of the gasoline from which olefine and aromatic hydrocarbons have been removed by the acid treatment is used for the estimation of the

paraffin and naphthene hydrocarbons, by reference to the curve, *Fig.* 2.

The gasoline is characterised by the temperature at which 50 per cent. has distilled over, called the *mid-point*, and a series of lines, ranging from 95° C. to 135° C., are shown on this curve, from which the percentage of paraffin and naphthene hydrocarbons may be seen.

The percentages shown are by weight on the olefine and aromatic hydrocarbon free gasoline, and will, of course, be less on the original gasoline. The percentage in the original gasoline is calculated from

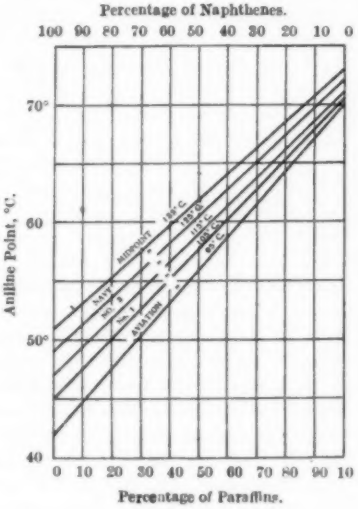

FIG. 2.

the percentage of olefine + aromatic hydrocarbons present. The figures on which this method of analysis is based are given later under aniline points of pure hydrocarbons (page 712).

EXPERIMENTAL METHODS.

1. ANILINE POINT.

The aniline point is determined on a mixture of equal volumes of the gasoline and freshly distilled dry aniline, preferably 5 cc. of each. The temperature of solution of this mixture is found by warming until the two layers disappear: the solution is then allowed to cool until a slight turbidity appears. The temperature

at which this occurs is the Aniline Point. It is advisable to repeat the operations of warming and cooling several times, and it will be found that the aniline point can readily be determined within 0.1° C.

Where the difference in aniline point before and after acid treatment is greater than 25° C., it is advisable to determine the aniline points of a mixture of equal volumes of aromatic free petrol and the gasoline before treatment, and of a mixture of equal volumes of the same aromatic free petrol with the acid-treated gasoline. The difference in aniline points gives the percentage by weight in a 50 per cent. by volume mixture. The percentage weight in the original gasoline is easily calculated if the specific gravity of the aromatic free gasoline is known.

2. Iodine Number.

Solutions :—

Iodine Solution.

Iodine	25·4 grams
Bromine	5·8 c.c.
Glacial Acetic Acid	2,000 c.c.

Decinormal Sodium Thiosulphate Solution Potassium Iodide Solution.

Potassium Iodine	100 grams
Distilled Water	1,000 c.cs.

Starch Solution.

Iodine Solution.—The iodine solution is conveniently and rapidly made up as follows : A small piece of glass wool is placed in the bottom of a glass funnel and the latter placed in the mouth of a Winchester quart bottle (2½ litres capacity). The glacial acetic acid is measured in a litre flask and transferred to conical flasks as required. The latter are warmed by immersion in hot water and the hot acetic acid poured through the iodine which is supported by the glass wool in the funnel. In this way the iodine is rapidly dissolved and the bromine is then measured out and added to the solution of iodine when the latter has cooled. It is not essential that the proportions shall be absolutely exact, although, of course, it is desirable that no great divergence from these quantities shall be used. The iodine solution does not appear to alter if kept in the dark, even after three or four months. It is essential that the acetic acid shall be pure as otherwise erratic iodine numbers are obtained.

Method.—The iodine solution is standardised periodically in the regular determination of iodine numbers by a blank determination—that is, by titrating the mixture as described below, but without the addition of the gasoline. Where the method is used in routine work each operator should find his own blank as slight difference in the method of procedure—*e.g.*, in the measurement of the iodine solution will give slightly different figures, although the calculated iodine number will be the same.

In general, where great accuracy is not necessary, the gasoline can be measured instead of weighed, and for this purpose the pipette devised by E. W. Dean* is excellent. This pipette consists of a piece of capillary tubing with drawn-out point for which convenient dimensions are : bore 1·5 mm., length 35 cm. Calibration marks showing the following volumes are etched on the pipette—0·6, 0·4 and 0·2 cc.

Wide-mouthed bottles (stoppered) and of about 400 ccs. capacity are used for the determinations.

Ten cc. of carbon tetrachloride is placed in the bottle, a definite volume of the gasoline is measured out and run into the carbon tetrachloride from the pipette and washed out by drawing the carbon tetrachloride twice into the pipette, each time allowing to drain. Where the temperature differs greatly from 60° F. the temperature of the gasoline is taken, as the iodine number is based on the *weight* of gasoline used. As the method is, however, only accurate to about 2 per cent., the temperature correction can usually be neglected.

Twenty cc. of the iodine solution is now added and the pipette allowed to drain until one drop of the iodine solution has fallen into the bottle after the pipette has apparently emptied. The bottles are then placed in a dark cupboard for exactly fifteen minutes, 5 cc. of the potassium iodine solution is now added and the bottle shaken, about 200 cc. of distilled water added, and then standard sodium thiosulphate solution added from a burette until the solution is slightly yellow. It is necessary to shake the liquid vigorously as soon as the yellow colour fades on the aqueous layer in order to ensure that the iodine in the carbon tetrachloride at the bottom of the bottle may be removed. Starch solution is now added and thiosulphate solution again added carefully until the blue colour is just removed.

This method of determining iodine numbers is based on Faragher, Gruse and Garner's paper on the Hanus Solution (J.Ind. Eng. Chem., 1921, **13**, 1044).

Calculation of the Results.—The difference between the volume of sodium thiosulphate solution required in the iodine number determination and in the blank gives the amount of solution used up, and this corresponds to the weight of iodine absorbed by the gasoline.

$$\text{Iodine Number} = \frac{\text{cc. sodium thiosulphate used up} \times 1{\cdot}27}{\text{vol. of gasoline} \times \text{sp. gr. gasoline.}}$$

The specific gravity should be the specific gravity at the temperature at which the gasoline was measured out, but usually the

*Bureau of Mines Bulletin No. 181.

specific gravity at 60° F. can be taken as sufficiently accurate. For routine work, as in the control of cracking plants, the iodine number may be calculated by means of the alignment chart, Fig. 3, which is based on the above formula. Usually 0·4 or 0·6 cc. can

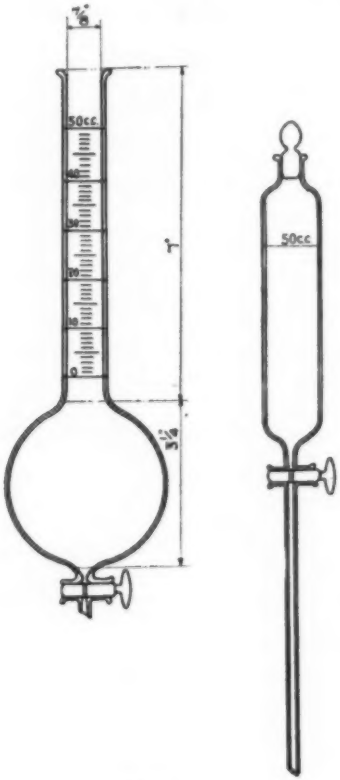

FIG. 4.

be adopted for cracked gasoline. The volume of gasoline should be chosen so that about one-third of the iodine solution only is used up—*i.e.*, if the blank shows 40 cc. of N/10 sodium thiosulphate solution, then the actual titration figure of the gasoline should be about 27 cc. Where the iodine number is to be used for the estimation of olefines, the following procedure is adopted. At least two

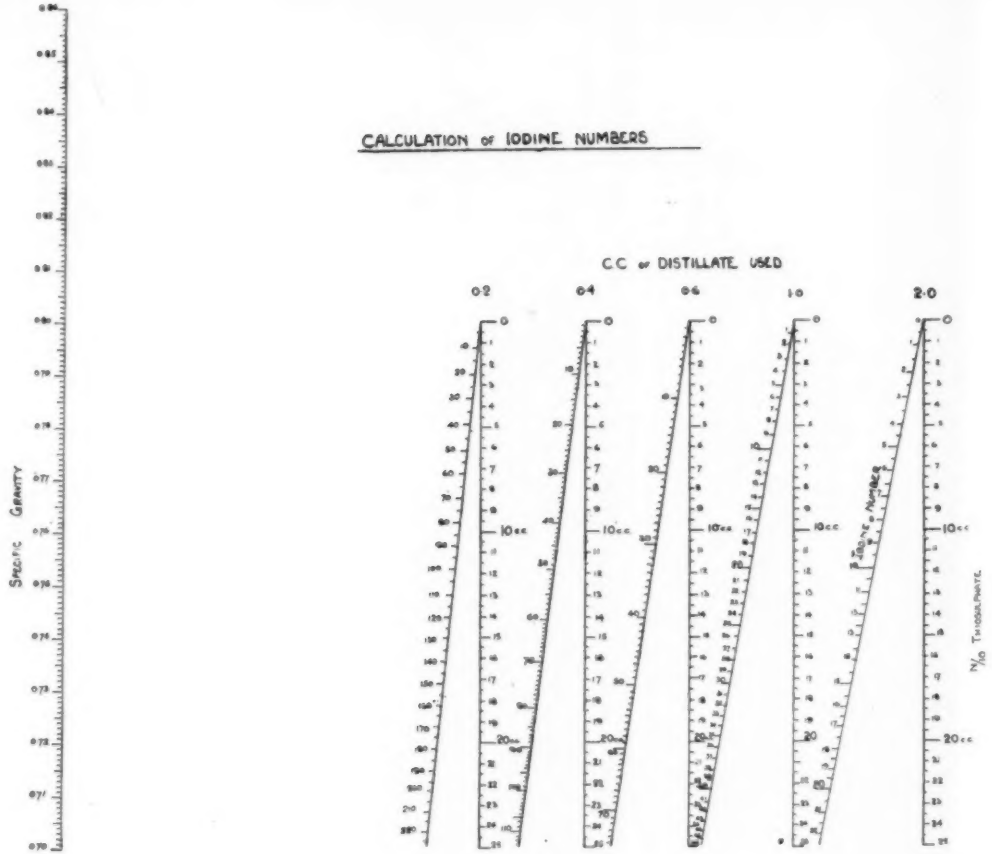
CALCULATION of IODINE NUMBERS
C.C. of DISTILLATE USED
0·2
0·4
0·6
1·0
2·0
SPECIFIC GRAVITY
IODINE NUMBER
N/10 THIOSULPHATE

FIG. 3.

determinations are made with different volumes of petrol and the iodine number is calculated for the titration figure corresponding to one-third of the blank.

With nearly saturated gasolines 0·6 cc. is used, and iodine numbers below 5 are taken as saturated and free from olefines.

Where great accuracy in the iodine number is necessary the gasoline may be weighed, but it is doubtful whether this presents any advantage for cracked gasolines since the olefine content does not bear an exact relation to the iodine number.

3. Removal of Olefine and Aromatic Hydrocarbons by means of Fuming Nitric Acid.

The apparatus for this purpose has been specially devised and consists of a separating funnel to measure the gasoline and a separating funnel in which to carry out the reaction. The latter consists of a spherical portion attached to a long stem graduated in ccs. from 0 to 50. The dimensions are shown on Fig. 4. To protect the stopcock during the shaking operations a piece of cork is cut to suitable shape, fitted around the stopcock and the lower part of the bulb and then wired to the upper part of the separating funnel.

In use, the spherical portion of the funnel is kept immersed in a freezing mixture, and the shaking performed by an up and down movement rather than side to side shakings. *It will be appreciated that the temperature of the fuming acid and gasoline must not be allowed to rise as otherwise a violent reaction may take place.* If, however, the temperature of the freezing mixture is kept at − 5 to − 10° C., and a short time allowed for the nitric acid to cool before commencing the addition of the gasoline, there is no danger whatever even with cracked spirits containing 50 per cent. of olefines. Such a high percentage is only met in vapour phase cracked gasolines. Apparently, if the temperature is kept low, the olefines simply add on nitric acid, giving nitro-compounds which are stable at these low temperatures. The test should always be carried out in a fume cupboard with a good draught. Although the operation might be expected to be somewhat hazardous in the case of highly cracked spirits, this method has now been used for considerably over a year now without any development of nitric acid fumes, except where the mixture of nitric acid and olefines was deliberately allowed to warm up.

Into the large, clean dry separating funnel is poured 125 cc. of fuming nitric acid, and this is cooled in a freezing mixture of ice and salt which is at − 10° C. for ten minutes. 50 cc. of the gasoline is then measured out in the other funnel and allowed to run slowly into the nitric acid: the latter is constantly shaken during the

addition so that intimate contact is effected between acid and gasoline. At least half-an-hour should be taken to add the gasoline, and a final shaking given after all the gasoline has been added. Time is allowed for the spent nitric acid to settle out, when the acid is separated from the gasoline by means of the stopcock, and run to waste into a vessel containing water. The gasoline is then washed three times with 20 cc. of nitric acid (fuming), in order to remove any nitro-compounds which may be dissolved in it: each time a fairly vigorous shaking takes place after the addition of the acid. After the nitric acid treatment is completed, a little water is added and shaken with the gasoline. Further water is then introduced carefully through the stopcock through a piece of rubber tubing until the gasoline is displaced into the stem of the separating funnel, and this volume of petrol is then carefully measured. The oil is further washed with dilute caustic soda solution and water, and should be sweet smelling and quite free from nitro-compounds. The specific gravity and aniline point are determined on the dry oil. In order to find out what is the mechanical loss during treatment, a blank should be carried out on 50 cc. of aromatic and olefine free petrol; the loss should not exceed 2 per cent., and this figure should be added to the experimentally determined volumes after treatment in every case. At least two determinations on each cracked spirit should be made, and these should not differ by more than 1 per cent.

Explanation of the Procedure Adopted in Methods of Analysis.

It will be noticed that percentage loss in volume is used for the calculations instead of loss by weight. Where there is little difference between the specific gravity before and after treatment, there is similarly little difference between these two percentages: where there is a marked difference, it has been found that the loss experimentally determined is greater than the real loss due to the removal of aromatic and olefine hydrocarbons, and that in these cases the experimentally determined loss in *volume* is approximately equal to the real loss in *weight*. The treated gasoline is slightly soluble in the fuming nitric acid and nitro-compound mixture, and this solubility apparently increases with increasing percentage of nitro-compounds. The error due to this increased solubility is thus counter-balanced by taking loss in volume instead of loss in weight.

Method No. 1.—It was found experimentally that the olefines in cracked spirit lower the aniline point approximately 2/5 of the extent produced by the same percentage weight of aromatic hydro-

carbons. Hence, if A = percentage of aromatic hydrocarbons, and B = percentage of olefines, a = aromatic hydrocarbon equivalent determined from Fig. 1, by difference in aniline point, and b = experimentally determined percentage loss in volume, then :—

$$A + 2/5\ O = a.$$
$$A + O = b.$$
$$\text{Or } O = 5/3\ (b—a)$$
$$\text{and } A = b—O,$$

which is the basis of Method No. 1.

Inaccuracy in the determination of the loss in volume introduces a greater error into the olefine percentage than the aromatic hydrocarbon percentage.

The olefine percentage may be determined from the iodine number, and should check up with the figure calculated by Method No. 1 in general to within ± 1.

Method No. 2.—With great care, the loss in volume can be experimentally determined to within 1/4 cc., which means that the estimated loss in volume is determined to within ± ½ per cent. It should be noted that this ± ½ per cent. is a positive error, and not ± ½ per cent. of the percentage loss in volume. Usually, however, the error will be somewhat greater. In Method No. 1, the olefine content is the difference between 5/3 of the loss in volume, and the aromatic hydrocarbon equivalent, or a possible error of ± 1·0 per cent. in the olefine content is possible. Thus, if Method No. 1 were used with cracked gasolines of low olefine content, the percentage error would be very great. In Method No. 2, instead of using 5/3 loss in volume, the olefine content is estimated by means of the iodine number, and as already explained, for heavy spirits the iodine number of a spirit with 100 per cent. olefines would vary from 260–290, or for 10 per cent. olefines from 26–29. With an iodine number of 25, the olefine content may be from 8 to 9·5, or a possible error of 1·5 per cent. in the olefine content, which is lower than that inherent in Method No. 1. Hence, with cracked spirits of iodine number 25 or under, it is recommended that Method No. 2 be employed rather than Method No. 1. Gasolines of high aromatic hydrocarbon content tend to give somewhat erratic results in the determination of loss in volume owing to the solubility of the treated gasoline in the nitric-nitro compound mixture, and hence in Method No. 2 the loss in volume is not employed as a basis of calculation. The aromatic hydrocarbon equivalent and the iodine number determination (with the limits

mentioned) are determined and consistent results are much more easily obtained than in the loss in volume determination, and hence in Method No. 2 loss in volume is not used.

It is important to note that in the calculation of aromatic hydrocarbon equivalent, olefines and aromatics are taken together; aniline point difference plotted against percentage of hydrocarbons (curve 1) is not a straight line, so that the sum of the aniline point differences for A per cent. and B per cent. of aromatic hydrocarbons is not the same as for A + B per cent., and the same consideration applies to mixtures of aromatic hydrocarbons and olefines.

The Action of Sulphuric Acid on Cracked Spirit.

Aromatic hydrocarbons behave as though they were slightly unsaturated and olefines vary considerably in their reactiveness to different reagents, and so far no reagent has been discovered that will completely remove olefines without at the same time removing also at least part of the aromatic hydrocarbons present. We have investigated a number of reagents of different types such as bromine, hypochlorous acid, potassium permanganate solution, and stannic chloride, without finding one suitable for analytical purposes.

It is possible to use bromine under such conditions that the olefines will be converted to dibromides without the formation of bromo-derivatives of the aromatic hydrocarbons to any appreciable extent, but it is not possible to separate the dibromides from the unattacked hydrocarbons. The dibromides of the lower olefines can be steam-stilled without appreciable decomposition, but in the case of the higher dibromides (derived from hexylene or higher boiling point olefines), decomposition occurs to an increasing extent with increasing molecular weight: steam distillation of a cracked spirit treated with bromine, thus, not only splits off hydrogen bromide but carbonisation also takes place and a discoloured distillate is obtained. This distillate contains, besides the paraffin, naphthene, and aromatic hydrocarbons present in the spirit, olefines and olefinic dibromides formed by the elimination of hydrogen bromide from the olefine dibromides. The distillate is of a more complex composition than the original spirit.

The low reactivity of the higher olefines, and the instability of the addition compounds which they form, render the separation of olefines from aromatic hydrocarbons very difficult.

Sulphuric acid has been used as an approximate method for the estimation of olefines in cracked spirit although it is recognised that the resulting treated oil contains polymers, so that the actual olefine content is higher than that measured by loss in volume. Attempts have been made to determine the proportion of polymers

by distillation to a lower end-point than that of cracked spirit. This method is used in the approximate method of analysis of Egloff & Morrell (*J. Ind. Eng. Chem.*, 1927, **18**, 354), but does not give accurate results because the polymers from the lowest boiling olefines present distil below 150° C., which is much below the end-point of the average cracked gasoline. A further objection to the use of sulphuric acid, where aromatic hydrocarbons are also estimated, is that this reagent not only removes olefines, but also aromatics (Garner, *J. Inst. Pet. Tech.*, 1926, **12**, 66 ; Brame, Ibid, 221). Attempts have been made by Brame (*J. Inst. Pet. Tech.*, 1926, **12**, 221), with 85 per cent. and 88 per cent. sulphuric acid, but it was found that even with these dilutions, condensation of olefines and aromatic hydrocarbons take place in accordance with the reaction discovered by Brochet (*Bull. Soc. Chim.*, 1893, **9**, 867), thus with the 85 per cent. sulphuric acid about 30 per cent. of the aromatic hydrocarbons used was found to be removed. Ormandy in a number of recent papers has also shown the complicated nature of the reaction between sulphuric acid and cracked spirit.

Even with 98–100 per cent. sulphuric acid, as used in the Institution of Petroleum Technologists Standard Method for the estimation of aromatic hydrocarbons (which is limited to the analysis of straight-run petrols), the treated portion of a cracked spirit does not correspond with the paraffin and naphthene content of the spirit ; removal of the olefines and aromatic hydrocarbons and *their reaction products* is not completely effected even with this concentration of acid. It is known that more highly concentrated acid will attack the naphthenes present in gasolines.

If various percentages of pure aromatic hydrocarbons are added to a cracked gasoline, and the olefinic and aromatic hydrocarbons simultaneously removed from these mixtures by suitable treatment, then if no side reactions have occurred the specific gravity and aniline points of the treated portion should be the same from all the mixtures. Actually, with sulphuric acid (in the I.P.T. method) the specific gravity is higher and the aniline point is lower, the higher the percentage of aromatic hydrocarbons added.

	Original Cracked Petrol.	+10% Benzene.	+20% Benzene.
Specific gravity at 60° F.	0·7405	0·751	0·762
Aniline point	51·5° C.	44·2° C.	35·3° C.
After treatment with sulphuric acid, I.P.T., G30.			
Specific gravity at 60° F.	0·7395	0·7435	0·7455
Aniline point	65·8° C.	64·0° C.	63·0° C.
After treatment with fuming nitric acid.			
Specific gravity at 60° F.	0·7305	0·7305	0·1573
Aniline point	64·5° C.	64·7° C.	74.6 ·C°

The fuming nitric acid treatment gives gasolines with substantially the same specific gravities and aniline points for all three spirits, so that these figures may be assumed to correspond with the paraffin and naphthene hydrocarbon content of the original petrol.

With sulphuric acid and cracked spirit two reactions occur :—

(1) Polymerisation, giving products of higher specific gravity and aniline point than the original spirit.

(2) Condensation of olefines and aromatic hydrocarbons to give products of higher specific gravity and aniline point than the original spirit.

The products of these reactions are not completely removed by the sulphuric acid treatment, with the result that the specific gravity of the acid-treated spirit is always higher than that of the paraffin and naphthene portion of the cracked spirit, but the aniline point is sometimes higher and sometimes lower after the treatment, depending whether the aromatic hydrocarbon content is high or low.

There are thus two fundamental sources of errors in the sulphuric acid method for the analysis of cracked spirits :—

(1) Olefines and aromatic hydrocarbons are removed and simultaneously addition products formed, so that the loss in volume does not give a true indication of the olefine and aromatic hydrocarbon content.

(2) The treated portion of the cracked spirit is not the same as the paraffin and naphthene portion of the cracked spirit, with the result that the properties of this acid-treated spirit cannot be used for the estimation of the paraffin and naphthene contents.

Fuming Nitric Acid and Cracked Gasoline.

It is, unfortunately, not possible to duplicate a cracked gasoline by making a mixture of synthetic hydrocarbons of the different series owing to the large number of individual hydrocarbons which would be necessary for this purpose. It was, therefore, decided to make a nearly aromatic-free gasoline by cracking a paraffin base crude petroleum and adding to it various proportions of aromatic hydrocarbons.

Hardstoft crude petroleum contains, even in its higher boiling fractions, lower percentages of aromatic hydrocarbons and higher percentages of paraffins than Pennsylvanian crude and was, therefore, suitable for this purpose. The crude, topped to remove gasoline and part of the kerosine, was cracked at a relatively low pressure (100 to 150 lbs. per sq. inch) and the resulting cracked

distillate refined to give a gasoline with 30 per cent. over at 100° C. and 185° C. end-point. To this refined gasoline of iodine number 120, aromatic free gasoline of similar distillation range was added, and gasolines of iodine numbers 74 and 48 were obtained with, of course, much lower aromatic hydrocarbon content. By analysis, 0 and 1·5 per cent. of aromatic hydrocarbons were found in these mixtures. These iodine numbers correspond to gasolines on the market of fairly high cracked spirit content (the iodine number of spirit from Cross units is about 60). From these mixtures blends were made with various proportions of aromatic hydrocarbons, and these were analysed by the method already described on p. 697. The results on one of these series of blends is given in the following table :—

	Olefines.	Aromatic Hydrocarbons. Found.	Calculated.
Original	19% ..	0·5% ..	—
5% Benzene added ..	17% ..	6% ..	5·5%
10% „ „ ..	16·5% ..	10% ..	10·5%
20% „ „ ..	15% ..	20% ..	20·5%

Attempts have been made to utilise the nitro-compounds, formed by the nitric acid treatment, for the estimation of the aromatic hydrocarbons present. As, however, has been pointed out, the olefines form addition compounds with the nitric acid, and these on further nitration give a certain proportion of solid tri-nitro-compounds which are not readily distinguishable from those derived from aromatic hydrocarbons. The stability of these nitro-compounds was much greater than expected.

A number of experimental results obtained at different times with this method of analysis follow :—

Cracked petrol from vapour phase cracking.

Iodine number, 145.

Olefines, 58 per cent.

Aromatic hydrocarbons, 17 per cent.

Mixtures of cracked gasoline and olefine and aromatic free gasoline.

Cracked.	Aromatic Free.	Olefines. Found.	Calculated.	Aromatic Hydrocarbons Found.	Calculated.
100% ..	0% ..	42% ..	— ..	15% ..	—
75% ..	25% ..	33% ..	31·5% ..	11% ..	11%
50% ..	50% ..	21·5% ..	21% ..	7% ..	7·5%
25% ..	75% ..	11% ..	10·5% ..	5% ..	4%

All the following gasolines are No. 1 grade, about 40 per cent. over at 100° C. and about 180° C. end-point.

	Olefine.	Aromatic.	Naphthene.	Paraffin.
High pressure cracking of naphthene base kerosene	24%	9%	35%	32%
Scottish Shale Petrol. Sp. Gr. at 60° F. 0·718. Iodine No. 100 ..	39%	8·5%	9%	43·5%
Naphthene base residue cracked at 150. Sp. Gr. at 60° F. 0·730. Iodine No. 110	36·5%	6·5%	11·5%	46%
Mixed Base Crude.				
Light Gas Oil cracked at 150 lbs./sq. in.	30%	8·5%	15%	46·5%
Heavy gas oil cracked at 150 lbs./sq. in.	41%	6·5%	9%	43·5%
Residue cracked at 150 lbs./sq. in. ..	45%	6%	8%	41%

As a final test of the method paraffin wax of melting point 126° F. was cracked at 150 lbs. per sq. inch, and a refined gasoline with 35 per cent. distilling over at 100° C. was made from the cracked distillate. This gasoline was expected to consist almost entirely of paraffin and naphthene hydrocarbons.

The analytical results by method No. 1 are as follows :—

Experiment No.	Sp. Gr. 60° F.	Loss.	Aniline Pt.	After Treatment. Sp. Gr. 60°F.	Aniline Pt.
1	0·712	49%	50·4° C.	0·7075	68·8° C.
2	0·712	49·2%	50·4° C.	0·7075	68·9° C.

Iodine Number 134.

Experiment No.	Olefines.	Aromatic.	Naphthene.	Paraffin.
1	47·5%	1·5%	3·5%	47·5%
2	47·5%	1·5%	3·5%	47·5%

No polymerisation occurred in the nitric acid treatment as redistillation gave 90 per cent. distillate of almost identically the same specific gravity and aniline point as before distillation. The iodine number of the treated petrol was 1, showing complete absence of olefines. By calculation the specific gravity and aniline point of the combined aromatic and olefinic hydrocarbons present in the cracked gasoline were found to be 0·717 and 32° C. respectively. Assuming 0·875 for the specific gravity of the aromatic hydrocarbons present, we have the specific gravity of the olefines as 0·712 as compared with 0·708 for heptylene and 0·724 for octylene.

The residue from which the above gasoline was distilled was further submitted to cracking and gave a gasoline of the following composition :—

Olefines, 47 per cent.
Aromatics, 1 per cent.
Naphthenes, 10·5 per cent.
Paraffins, 42 per cent.

There is thus an increase in the percentage of naphthenes in this product of a re-cracking operation. It is interesting to note that both naphthenes and aromatic hydrocarbons are produced by cracking paraffin wax, even at this relatively low pressure.

Mixtures were made up of :—

1. Cracked gasoline from paraffin wax.
2. This gasoline after treatment with fuming nitric acid.
3. Pure benzene.
4. Gasoline containing 14 per cent. of aromatic hydrocarbons, 26 per cent. naphthenes and 60 per cent. paraffins.

Mixture No. 1.

	Calculated Composition.	Found. Method No. 1.	Method No. 2.
Olefines	23·0%	24·5%	22·2%
Aromatics	23·5%	23.0%	24·3%
Paraffins	44·5%	44·5%	45·0%
Naphthenes	9·0%	8·0%	8·5%

Loss in volume :—Calculated, 46·5 per cent.
Found, 47·5 per cent.

Aniline point of aromatic and olefine free gasoline :—
Calculated, 67·0° C.
Found, 67·5° C.

	Before treatment.	After treatment
Specific gravity 60° F.	0·7455 ..	0·715
Iodine Number	60 ..	2
Aniline point	35·8° C. ..	67·5° C.

Mixture No. 2.

	Calculated Composition.	Found. Method No. 1.	Method No. 2.
Olefines	15·0%	15·0%	14·5%
Aromatic hydrocarbons ..	17·5%	17·5%	18·0%
Paraffin „ ..	55·0%	54·0%	54·0%
Naphthene „ ..	12·5%	13·5%	13·5%

Loss in volume :—Found, 32·5 per cent.
Calculated, 32·5 per cent.

Aniline point of olefine and aromatic free gasoline, 66·5° C.

	Before treatment.	After treatment.
Specific gravity at 60° F.	0·7385 ..	0·7195
Iodine number	39 ..	1
Aniline point	44·6° C. ..	66·5° C.

In these instances there is an agreement between the two methods of analysis: where naphthene base crudes are cracked the iodine number is not a reliable method as a basis for analysis for the more highly unsaturated spirits, for substitution occurs as well as addition.

Consequently, where naphthenes are present in any large proportion, method of analysis No. 2 may give inaccurate results where the iodine number is over 25.

The method of analysis described in the preceding pages is not claimed to be as accurate as could be desired: for example, the percentages of paraffins and naphthenes cannot be determined accurately without a very complicated procedure. It is, however, put forward as a rational method of analysis which will give consistent results with an accuracy probably within 1 of the correct figure. This accuracy is sufficient for correlating with engine tests.

The Aniline Points of Pure Hydrocarbons.

The aniline point of all pure hydrocarbons corresponds very closely to the Critical Solution Temperature, and in the discussion which follows, a certain equality of the two terms is assumed.

Chavanne and Simon, who originated this method of the analysis of hydrocarbons, give the temperature of critical solution of a number of hydrocarbons, and in later papers they and their co-workers have given other figures. In the tables which follow, the results of Chavanne and Simon, together with results obtained by the author, are summarised.

In many cases the hydrocarbons were obtained from Kahlbaum or Eastman-Kodak, and were assumed to be pure, but quite a large proportion of the hydrocarbons were specially prepared for this purpose and their physical constants were found to be the same as the most authoritative figures in the literature.

It can be assumed that in general, the aniline points of mixtures of hydrocarbons follow the straight line law, but this is not the case where the difference between the aniline points of the hydrocarbons is very great, as with mixtures of aromatic and other hydrocarbons.

A large number of mixtures of individual naphthene and olefine, or naphthene and paraffin hydrocarbons have been made up, and in every case the deviation from the straight line is so slight that it can be neglected in methods of analysis where other factors necessarily introduce such a large error.

For the paraffin hydrocarbons it is assumed that normal chain compounds predominate, as the evidence of fractionation available indicates that this is probably the case in most crude petroleums.

For naphthene hydrocarbons it is assumed that the naphthenes present in petrol are equally divided between the five ring and six ring series. From the point of view of detonation it has generally been assumed that the six ring series—cyclohexane, methyl cyclohexane, etc., are the only naphthenes present, but

the evidence available shows that the cyclopentane derivatives are present in approximately equal proportions with the cyclohexane series in the lower fractions of crude, but that with ascending boiling point, the cyclopentane derivatives predominate over the cyclohexane hydrocarbons. Figures are also given for bicyclic naphthene groups of hydrocarbons, which are present in the highest boiling fractions of gasoline in small proportions.[1] There is some evidence that the olefines present are not straight chain compounds entirely, but that ring olefines and branched chain compounds are also present. It should be noted that cyclohexene, a ring olefine, forms gum readily in storage, thus behaving in a similar manner to di-olefines.

The aromatic hydrocarbons curve, Fig. 1, is as devised by Tizard and Marshall,[2] who are responsible for the use of aniline point instead of the critical temperature of solution used by Chavanne and Simon.

The aniline points recorded below are principally by Chavanne and Simon and co-workers. Where no reference is given the results are obtained by the author.

PARAFFIN HYDROCARBONS.

Normal	Boiling point, ° C.	Sp. gr. at 60° F.	Aniline point, ° C.
Pentane	36·3	0·633	72·0†
Hexane	69·0	0·644	69·0†
Heptane	98·3	0·6885	71·0
Octane	125·5	0·7065	71·8†
Nonane	149·5	0·7215	74·5
Decane	175·5	0·734	77·5
Undecane	194·5	0·745	77–78ϕ
Tetradecane	252·5	0·768	88·0ϕ
Pentadecane	270·5	0·7725	92·0ϕ
Hexadecane M. Pt. 19° C.	287·5	0·7775	88·0

Iso and Tertiary.

No. of carbon atoms.		Boiling point, ° C.	Sp. gr. at 60° F.	Aniline point, ° C.
5	2-methyl-butane ..	31	0·625	77†
6	2-methyl-pentane ..	62	0·660	73·8†
7	2-methyl-hexane ..	90·5	0·693	72·8
7	3-methyl-hexane ..	91·8	0·691	70·5
7	Methyl-ethyl-isopropyl-methane	90	0·699	68·1
10	Diisoamyl	157	0·7355	79·0

ϕ Carpenter (*J. Inst. Petr. Techn.*, 1926, **12**, 562).
† Chavanne and Simon, C.r. 168, 1324, (1919) and subsequent papers.

[1] See for example Brame and Hunter, *J. Inst. Petr. Tech.*, 1927, **13**, 794.
[2] *J. Soc. Chem. Ind.*, 1921, **40**, 20T.

Naphthene Hydrocarbons.

Cyclopentane Hydrocarbons.

	Boiling point, °C.	Sp. gr. at 60° F.	Aniline point, °C.
Cyclopentane	50	0·756	18[1]
Methyl-cyclopentane	72	0·7535	35[1]
1.3.dimethyl-cyclopentane ..	91	0·749	45[2]
Ethyl-cyclopentane	103	0·771	39[2]
1.2.3-trimethyl-cyclopentane..	105·5	0·780	41
Propyl-cyclopentane	131·5	0·781	45[3]
Butyl-cyclopentane	157	0·789	50·5[3]

Cyclohexane Hydrocarbons.

	Boiling point, °C.	Sp. gr. at 60° F.	Aniline point, °C.
Cyclohexane	80·8	0·7825	31[1]
Methyl-cyclohexane	100·4	0·774	41[1]
1.2-dimethyl-cyclohexane ..	129·0	0·793	42·1[4]
1.3-dimethyl-cyclohexane ..	121·1	0·775	49·7[1]
1.4-dimethyl-cyclohexane ..	123.0	0·783	48·0[1]
1.2.4-trimethyl - cyclohexane (Kahlbaum)	140	0·786	53·6
1-methyl - 4 - isopropyl - cyclo-hexane (Eastman-Kodak)	169·5	0·799	56·5

[1] Chavanne and Simon, *loc. cit.*
[2] Chavanne and Simon, c.r **168**, 111, 1919; and Chavanne, *Bull. sci. acad. roy. Belg.* (5) **12**, 105, 1926.
[3] Chavanne and Becker, *Bull. Soc. Chem.*, 1927, **36**, 591.

Bicyclic Naphthenes.

	Boiling point, °C.	Sp. gr. at 60° F.	Aniline point, °C.
Decahydronaphthalene ..	190	0·885	34
Cyclohexyl-cyclohexane ..	239	0·881	12
Methyl - cyclohexyl - cyclo - hexane	250	0·878	15

Olefine Hydrocarbons.

The figures given below are only approximate: the *n*-hexylene and *n*-octylene are apparently impure. The heptylene and cetene correspond in iodine number and other properties with those of pure compounds.

Normal.

	Boiling point, °C.	Sp. gr. at 60 °F.	Aniline point, °C.
Amylene	36	0·665	14·5[1]
Hexylene	68	0·685	17[2]
Heptylene	96–97	0·708	36
Octylene (Eastman-Kodak)	121–124	0·742	26·5[3]
Cetene	274	0·784	68

[1] D. Konowalow, *Ann. Phys.* (4), 375, (1903).
[2] Brame and Hunter, *J. Inst. Petr. Techn.*, 1927, **13**, 794, gives 16·4° C. for hydrocarbon boiling at 62° C.
[3] The sp. gr. of this hydrocarbon is higher than that of normal 1 octene or 2 octene.

Iso.			
Trimethyl - ethylene (Kahlbaum)	32	0·715	10[4]
Symm. methyl-propyl-ethylene (Kahlbaum)	66	0·7035	18
Isohexene (mixture)	66	0·687	24
Cyclic.			
Cyclohexene (British Drug Houses)	83	0·818	−20
Tetrahydronaphthalene ..		0·975	below −20

[4] Brame (*loc. cit.*) gives 11° C.

Aromatic Hydrocarbons.

A large number of aromatic hydrocarbons have been investigated and it is found that the aniline point curve for benzene corresponsd closely with that for all the aromatic hydrocarbons present in gasoline. Very high boiling hydrocarbons, *e.g.*, cetyl benzene or naphthalene and its derivatives, cause less depression of the aniline point.

The following figures are taken for the paraffin and naphthene hydrocarbons present in gasolines of various grades. As the proportion of naphthenes always increases in petroleum fractions considerably with increasing boiling point, the naphthene portion of a petrol is of higher boiling point than the paraffin portion, and an attempt has been made to allow for this in the following figures. These figures have been taken from Fig. 5, showing the relationship between boiling point and aniline point for the different series of hydrocarbons.

Aniline Points of Paraffins and Naphthenes in various grades of gasoline :—

	50% at °C.	Paraffin °C.	Naphthene °C.
Aviation Gasoline	95 ..	70 ..	42
No. 1 Gasoline ..	105 ..	70.5 ..	45
No. 3 Gasoline ..	115 ..	71 ..	47
U.S. Navy Gasoline	125 ..	72 ..	49
,, ...	135 ..	73 ..	51

The aniline point curve, Fig. 2, for paraffins and naphthenes, is based on these figures as will be readily seen.

Note —In the analysis of benzole mixtures these mixtures are characterised by the distillation range of the petrol rather than by the distillation range of the mixture. This distillation range is determined sufficiently accurately on the acid treated petrol.

Iodine Number.

It has been shown by Faragher, Gruse and Garner[3], in the case of a number of olefines, that the iodine number as determined by the Hanus method, agrees with the theoretical amount required to saturate the hydrocarbon, and that no substitution of hydrogen

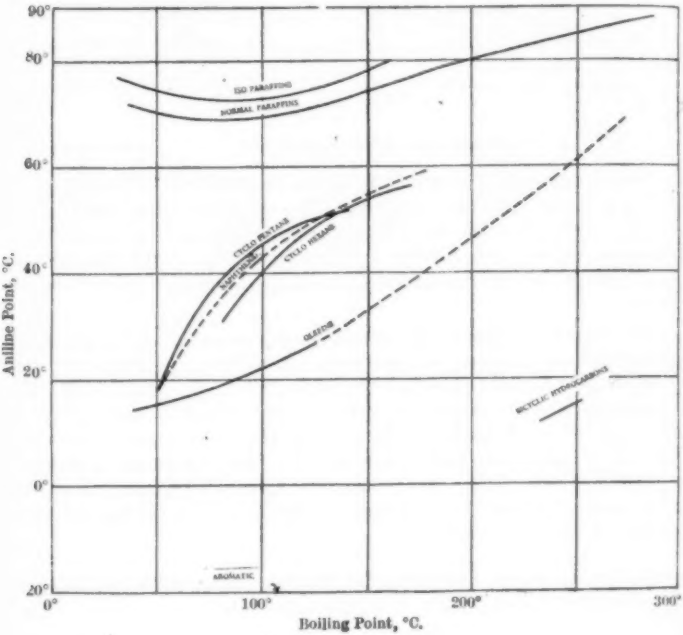

Fig. 5.

by halogen occurs. On the other hand, Johansen, by a modified McIlhiney method[4], found that with cracked petroleum products substitution did occur, with the result that the percentage of unsaturated compounds calculated from the iodine number, was in every case too high.

In the present paper, iodine number determinations of a number of olefines and one unsaturated sulphide, confirm the conclusions

[3] *J. Ind. Eng. Chem.*, 1921, **13**, 1044.
[4] *J. Ind. Eng. Chem.*, 1922, **14**, 288.

shown in the paper of Faragher, Gruse and Garner, and it is further shown that mixtures of olefines and normal paraffins follow the ordinary mixture law for iodine numbers, so that in these cases the iodine number can be used as a method for the estimation of the olefine content.

Further investigation of the substitution examined by Johansen shows that this is more marked with the solutions he employed than is the case with the Hanus solution, and confirms his conclusion that with the lower boiling fractions of a gasoline, substitution does not occur to any marked extent, but with the higher boiling point fractions, substitution takes place to an increasing extent. It seems improbable that the increase in substitution is necessarily connected with the presence of olefines or diolefines, since we find the same substitution occurs in the case of straight run products, and whereas in these products fractions distilling below 100° C. will have a negligible iodine number, fractions distilling over 100° C. have a definite iodine number which is due almost entirely to substitution since no olefines are present.

There is, in fact, no definite evidence of the presence of olefines or unsaturated hydrocarbons in any crude petroleum, and the recent work of Mabery[5], in the addition of bromine, indicates that the behaviour of the higher boiling lubricating oil fractions in petroleum, which are commonly called unsaturated, are in fact, saturated hydrocarbons of a cyclic structure.

At present we have no definite information as to the type of pseudo-unsaturated hydrocarbon which gives rise to these substitution values in the iodine number determination, but we know that normal straight chain hydrocarbons do not exhibit this property, and further, this particular type of hydrocarbon is removed by drastic refining methods. It seems probable that they are highly branched chain compounds, and that this substitution occurs in the higher derivatives of all classes of hydrocarbons, olefines, paraffins, naphthenes, and aromatic hydrocarbons.

It does not appear that all of the so-called substitution in petrols estimated by McIlhiney's method and Johansen's modification, is necessarily due to substitution of the hydrogen in the hydrocarbon by iodine.

The reaction between olefine and iodine can be represented as follows :—

$$R{-}CH_2{-}\overset{H}{C}{=}\overset{H}{C}{-}R_1 + I_2 = R{-}CH_2{-}\overset{H}{\underset{I}{C}}{-}\overset{H}{\underset{I}{C}}{-}R_1$$

[5] *J. Amer. Chem. Soc.*, 1927, **49**, 1116.

Where R and R_1 are large molecules, it appears that this type of compound can react with potassium iodate, giving iodine as follows:—

$$5R{-}CH_2{-}\underset{\displaystyle I}{CH}{-}\underset{\displaystyle I}{CH}{-}\underset{\displaystyle I}{R_1}+KIO_3$$

$$=5R{-}CH{=}CH{-}CH{-}R_1+3I_2+KOH+2H_2O$$

It is well known that the higher olefines are much less readily attacked by sulphuric acid and behave as much less unsaturated than the lower olefines. Similarly, it has been shown that the diolefines and acetylenes behave as simple olefines unless a large excess of iodine is present.

Thus, the iodine compounds formed from these higher olefines and diolefines are only stable in the presence of excess of iodine and readily split off hydiiodic acid, giving iodo-olefines. Comment has been made elsewhere in this paper (p. 706) on the fact that this reaction occurs with bromine.

If these conclusions are correct, part of the hydiiodic acid detected in Johansen's method is not due to substitution, and thus his figures for substitution are too high.

The theoretical iodine numbers of the olefine series which occur in cracked petrol are shown below:—

	Specific Gravity @ 60° F.	Boiling Point, °C.	Iodine Number
Butylene	— ..	1 ..	453
Amylene	0.665 ..	36 ..	363
n-Hexylene ..	0.685 ..	69 ..	302
n-Heptylene	0.708 ..	96 ..	259
n-Octylene	0.724 ..	122.5 ..	227
n-Nonylene ..	0.738 ..	141 ..	202
n-Decylene	0.751 ..	175 ..	181

Besides normal olefines there is no doubt that branched chain olefines and also cyclic olefines occur to some extent in cracked petrol, depending on the nature of the original distillate from which the cracked petrol is prepared, and in fact, the unsaturated components of a cracked petrol have always a much higher specific gravity than that of the corresponding normal hydrocarbons.

By plotting the above figures, iodine number against boiling point, we obtain a fair indication of the variation of iodine number of fractions from a completely unsaturated petrol. Actually the presence of cyclic olefines with two less hydrogen atoms than the

normal olefines will render these figures slightly too low, but the difference as the series is ascended becomes less.

Now by comparing the distillation range of a petrol carefully fractionated into fractions of say 10° C. boiling range, we can calculate what the iodine number should be if the petrol were completely unsaturated. From the iodine number of the petrol itself we can determine what is the percentage of unsaturated constituents present. Similarly, by comparison of the iodine number of the fractions with the iodine number shown in the olefine boiling point—iodine number curve, we can obtain some idea of the distribution of unsaturated constituents in the petrol as the boiling point rises.

Actually, this method is only of value with very light petrols, as at temperatures over 100° C. increasing substitution occurs giving, according to this method, fictitiously high olefine contents.

Thus, assuming no substitution occurs, we obtain the following iodine numbers for completely unsaturated petrol.

	% at 100° C.	50% at	Iodine Number. Calculated.	Observed.
Aviation	60	95° C.	260	260
No. 1	40	105° C.	245	270
No. 3	30	115° C.	220	270

Diolefines, if present, will give a lower iodine number than the theoretical figure, corresponding more or less to that of the olefine with a similar number of carbon atoms, and thus the iodine number method gives the total olefine and diolefine present. Usually, however, in refined spirits, to which the present method of analysis applies, diolefines are present in very small proportions.

Iodine Numbers of Pure Compounds.

The following results were obtained with hexylene, specific gravity 0.700, calculated iodine number 302.

Weight of Oil. grams.	Iodine Number.
0.122	249
0.115	247
0.05	317
0.0185	302
0.0199	319
5% Solution in olefine free petrol.	
Volume, c.c.	Iodine Number of olefine present.
2.0	314
0.4	308
10% Solution.	
2.0	300
0.6	307
0.4	299
50% Solution.	
0.4	289
0.2	312

Phenyl Acetylene, sp. gr. 0.9410.

Weight of Oil, grms.	Iodine Number.
0.199	223
0.22	225
0.105	238
0.0846	236
0.054	255
0.0334	269
0.0190	285

5% Solution in petrol with Iodine Number of 0.

Variation of Volume.

Time	Volume, c.c.	Calculated iodine number of Phenyl-acetylene.
¼ hour	0.2	340
¼ hour	0.4	310
¼ hour	0.6	295
¼ hour	2.0	255

Variation of Time.

Time.	Volume, c.c.	Calculated iodine number of Phenyl-acetylene.
¼ hour	0.2	340
½ hour	0.2	350
1 hour	0.2	380
2 hours	0.2	410

Calculated Iodine Number :

One molecule I_2 to $C_6H_5C \equiv CH$ .. 249
Two molecules I_2 to $C_6H_5C \equiv CH$ .. 598

Thus, it will be seen that under the ordinary conditions of determining the iodine number, this acetylene behaves as though it contained a double bond instead of a triple bond, and it is only when a very large excess of iodine is present, as in the 5 per cent. solution, that figures approaching the true unsaturation are obtained. These results confirm those with normal heptin in the figures of Faragher, Gruse and Garner.

Allyl Sulphide—Calculated Iodine Number 441.

Weight of Oil, Gms.	Iodine Number.
0.0796	380
0.0454	397
0.0158	402

Hexylene.

Symmetrical methyl propylethylene. Specific Gravity 0.7035. Calculated Iodine Number 302.

Weight of Oil, Grms.	Iodine Number.
0·28	144
0·14	248
0·070	288
0·035	310

Octylene (Eastman-Kodak), Specific Gravity 0·742. Calculated Iodine Number, 227.

Weight of Oil, Grms.	Iodine Number.
0·15	209
0·073	215
0·036	217

In general, the time during which the iodine solution and olefine are left in contact should be as short as possible as it has been shown that with true olefines the addition takes place in less than five minutes: on the other hand, the longer the time of contact, the greater the tendency for secondary reactions such as substitution to occur, as this is a much slower reaction. As will be seen, fifteen minutes has been adopted as the standard time in the method outlined.

Comparison of Johansen's method and the Hanus' Method described above.

	Weight of Oil, Grms.	Iodine Number. Johansen Addition.	Johansen Substitution.	Method p. 700
Hexylene	0·03	260	—	252
	0·06	250	—	250
	0·12	240	—	240
Heptylene	0·035	213	—	210
	0·065	180	—	180
	0·14	175	—	175
Cetene	0·07	120	—	120
	0·15	107	—	106
	0·28	101	—	102
Cracked Petrol—				
A	—	129	143	134
B	—	53	85	62
Petrol Fractions :—				
0— 60° C. ..	—	73	73	72
60— 90° C. ..	—	56·5	58·5	58
90—120° C. ..	—	45	61	49
120—150° C. ..	—	40	71	52
150—180° C. ..	—	32·5	53·5	37

The substitution which occurs in the carbon tetrachloride solution which Johansen used is seen to be greater than with the modified Hanus' solution, and the substitution increases greatly with increasing boiling point.

The iodine number obtained with the method described on page 700 is thus closer to the true addition number than would be obtained if carbon tetrachloride solution were used in the same way (*i.e.*, without applying the McIlhiney correction).

The author wishes to express his indebtedness to Mr. A. Osborn, who has carried out a large part of the experimental work described in this paper.

The President said the paper had been a very interesting one on one of the most complicated and difficult problems with which the petroleum chemist had to deal. There were a number of distinguished chemists present, and as the paper was essentially a chemical one, and one which should be dealt with by chemists, he would at once call upon Dr. Ormandy to open the discussion.

DISCUSSION.

Dr. W. R. Ormandy, in opening the discussion, said with a paper so complicated as that of Dr. Garner it was impossible to expect that anyone should be able to discuss it as it might be discussed after just hearing it somewhat cursorily read and after seeing large numbers of figures thrown on the screen. If he began by stating that he was commencing to doubt whether the work which was being done upon the subject of the analysis of cracked spirits was worth the time and energy which was being spent upon it, it must not be taken as being any imputation against the work of the lecturer. It was known to most present that the subject under discussion was one upon which he himself had spent a very large amount of time, but he was giving it up because he believed the problem was hopeless until such time as chemists were able to separate the individual ingredients out of the cracked spirit, and until they had isolated pure individuals and knew their properties. That part of the work, however, which dealt with the pure product was of real value, and a great debt of gratitude was owed to those who spent a large amount of time and money in isolating a number of pure paraffins, olefines, and other bodies in order that their chemical and physical properties might be properly studied. That was a line of research which deserved every encouragement.

He had once had the pleasure of talking to a very great philosopher in Germany, who, speaking of the works and systems of philosophy, had said, "If you want to study systems of philosophy, devote nine-tenths of your time to reading the first two chapters. It is where the premises are that the errors lay," and he (Dr. Ormandy) thought that that remark might be attached to some extent to Dr. Garner's paper. Those present were told that the method was in fact based on the separation of olefines and aromatics by means of nitric acid. If it could be shown that that same nitric acid, under the same conditions, acted upon paraffins or upon naphthenes, or upon both, then to a large extent the accuracy of the method was vitiated; and there was no doubt whatever that nitric acid did act, for instance, on methyl-cyclopentane, which was quantitatively oxidised by nitric acid, and there was the lecturer's admission that it was a body which was very frequently present in petrols.

The question arose why chemists were making these analyses? They were primarily to evaluate the petrol as a motor fuel. He took it that that was the main object of all the analyses. If there was any prospect of the analytical method being able to tell how that fuel was going to behave in a variable compression engine, then the work would be valuable; but, having regard to the work

of Edgar—who pointed out that taking the separate paraffins, when one went into the octane group from one to the other of the eight possible isomers there were greater differences there than there were between almost any paraffin and any naphthene, almost as great as between a paraffin and an aromatic—any physical or chemical method which merely distinguished the paraffins qua paraffins was, to that extent, valueless ; because unless it was known what paraffins were there, the mere fact that there was 46 per cent. of paraffin told chemists nothing. We were in a still worse position with regard to naphthenes as the number which had been isolated and studied was very much smaller.

He would like to ask the lecturer whether in fact his iodine method was merely Hanus' method slightly modified by taking a different length of time ? If that were so, he thought that one must deprecate the continuous addition of merely slightly modified processes. Chemists had now a horrible time in front of them in trying to keep track of the empirical methods ; and to keep on increasing them by varying one factor or the other was, he thought, only making the chemist's life more of a misery than it was at present.

With regard to the action of sulphuric acid on olefines and benzine, Craven and himself had shown perfectly definitely that arylation of the separated paraffins occurs in many cases but by no means invariably. For example with propylene and benzene sulphonic acid, propyl benzene sulphonic acid is formed and only very small amounts of what the author calls polymers but which are really open chain paraffins. Where arylation occurs naturally the specific gravity rises and aniline point falls. If no arylation occur, as for example where aromatics are not present, naturally the specific gravity and aniline point both rise owing to the heavy paraffins formed.

A very large proportion of the deductions which the author had drawn were deductions which one could draw by merely knowing the facts, namely, that when one treated an unsaturated with sulphuric acid one almost invariably obtained a range of heavy paraffins boiling from 90 to 360, and that in very many cases, if there were any aromatics present, they combined with the paraffins. All the rest of the conclusions flowed from that.

With regard to the action of nitric acid, there was no doubt that cyclo-pentane and methyl-cyclopentane were acted on by fuming nitric acid in the cold. They could be quantitatively oxidised as a matter of fact.

With regard to the use of the aniline point method for determinations in general, personally he was very averse to the use of the aniline point method for one reason, namely, the difficulty

which was attached to getting an aniline which was really water-free. If one was going to use an aniline point method it was absolutely essential that the aniline should be standardised against a standard paraffin or a standard chemical. Then the trouble arose that two people who were working on the same line did not compare their aniline against the same chemical. He thought that a great deal more should be done by taking advantage of the relationship between densities and refractive indices which he had found a more reliable method than the aniline point determination.

He should be very sorry if the lecturer thought that he desired to decry or lessen in any way the value of the work he had done, but personally he did think that it was essential that it should be realised that no method of analysis of cracked spirits was yet capable of displacing what was, after all, a very much shorter and easier thing, namely, to test the spirit in a variable compression engine. He seriously asked whether it was worth the enormous complication that was being entered into, when it was known that the fundamental facts were so vastly against a really satisfactory conclusion being reached, and whether it had not be better given up as a bad job, and whether the one good empirical test—namely, trying it in an engine—should not be relied upon.

Dr. A. E. Dunstan said he was inclined to associate himself with Dr. Ormandy's remarks, more particularly in reference to the value of the knowledge of the components of a cracked spirit. Personally, he thought that all the information which had been obtained (and it had been considerably added to within the last few years) indicated that it was not so much the paraffin content as the kind of paraffin content, and that it was not so much the naphthene content as the kind of naphthene content that mattered. He asked himself whether any good purpose was served, or whether any prediction whatsoever could be made, by it being known that analysis showed a high content of paraffins. There might have been some objection to using an engine test in the days when there had been only one or two engines in the country of the original Ricardo type; but there were now available quite a number of simple experimental engines from which one could get in the course of half an hour a definitely accurate statement of the value of a given fuel. That appeared to him to invalidate very considerably the highly complicated method of analysis mentioned by the lecturer.

There were a few points in the paper to which he would like to refer—first of all, the fuming nitric acid treatment, which was novel. He wondered how that kind of treatment would operate in the case of some of the cracked spirits that some members present

would remember had been made in 1916 in the days of synthetic toluol—spirits that would react with strong sulphuric acid with explosive violence, and that would even on dry distillation explode in the flask. He would like to hear the lecturer's view as to how those high-temperature cracked spirits would react with fuming nitric acid even at —5°C.

Mr. Harold Moore remarked that he would like to help to defend Dr. Garner against Dr. Ormandy's and Dr. Dunstan's remarks by stating that he did not think the value of the analyses mentioned had to be looked upon solely as a measure of the anti-knocking properties of spirit. Chemists wanted to know what was in cracked spirit for other reasons than knowing the value of it as an anti-detonator. They wanted to know the mechanism of the cracking reaction, and if they could get even rough figures which would lead them to know how much unsaturateds, and how much naphthenes, and so on, there was present, it would be of the greatest use to anyone operating a cracking plant. That was a point quite outside of spirit valuation.

There was one point on which he would like to raise a criticism against all the people who had written papers on the subject, including himself—namely, that they had all used the terms "unsaturated," "naphthene," "olefine" and "paraffins" as if those were very definite terms. They might be definite at the low boiling end, but when one got to temperatures towards the end point of U.S. Navy gasoline one had to realise that it was possible to get bodies of mixed composition. One might conceive the existence of unsaturated naphthenes, also unsaturated aromatics. Further, he would imagine that tetrahydro-naphthalene was not altogether an aromatic, and that it might be considered as partly naphthene. Even ethyl-benzene might be considered as having a little bit of the paraffin about it at one corner : it may be considered as an ethyl derivative of benzene or as a phenyl derivative of ethane. Such criticism might be applied to quite a number of compounds.

Dr. Garner had referred to a fully cracked spirit as 100 per cent. unsaturated. He would like to ask Dr. Garner whether he found with regard to a fully cracked spirit—a spirit which had been made from some heavy product and contained no products which had passed through the process without being cracked—that the analysis of the resulting fully cracked spirit usually approached a content of 50 per cent. unsaturateds and 50 per cent. paraffins when the original body was purely paraffin. The writer had observed from his own analyses of cracked spirit that when a pure paraffin was cracked the reaction appeared to follow the lines of that given in the text books—namely, a large paraffin molecule is cracked down into two

smaller molecules, one being unsaturated and the other saturated. Whether that applied for the cracking of naphthene it was difficult to say, but he noticed that the figures given on the last page of the paper very much indicated that Dr. Garner's results confirmed this view. He referred to an analysis of cracked spirit obtained from kerosine. This analysis gave 24 per cent. of olefines in the spirit. Assuming that that was cracked in a liquid phase cracking plant of the ordinary type, he should imagine that about half of the spirit would consist of uncracked products which had simply been fractionated from the charging stock: that was to say, half of the spirit was not a cracked body but purely a body obtained by fractionation from the lower boiling products present in the charging stock. In the case of the paraffin wax, which would be entirely free from light products, one got 47 per cent. of paraffin and 47½ per cent. of olefines, which was getting very close to the fifty-fifty figure.

Dr. F. B. Thole expressed the opinion that Dr. Garner had, in his nitric acid method for the separation of olefines and aromatics from paraffins and naphthenes, made an important and valuable step forward in the problem of analysing a cracked spirit into chemical grades, for while it was now universally recognised that no strength of sulphuric acid was capable of removing olefines and their resultant derivatives (polymers or esters) from such a spirit, Dr. Garner produced convincing evidence that nitric acid treatment under controlled conditions had accomplished this satisfactorily.

As regards the calculation of the paraffin-naphthene ratio of the resultant spirit from the aniline point and mid-boiling point, by reference to the curves shown in Fig. 2, he felt less satisfied, as the curves themselves were not very accurate approximations, and a number of assumptions had to be made which might or might not be true. He would be glad to know what the plus and minus error in such an estimation was likely to be. After all, the only convincing evidence as to the value of a proposed method of analysis, was to test it on a number of mixtures of known composition made from substances of irreproachable purity, and he would be glad not only to see such evidence before altogether accepting the method, but also to supply Dr. Garner with such mixtures.

As regards the practical value of knowing the percentages of aromatics, olefines, naphthenes and paraffins in a spirit, he was inclined to agree with Dr. Ormandy and Dr. Dunstan that it was but small in view of the fact that the label "paraffin" or "naphthene" or "olefine" gave no indication of the value of a motor spirit as an engine fuel. From one important standpoint alone, that of pinking tendencies, some paraffins were extremely bad and others extremely good, and similar remarks applied to olefines and

perhaps to naphthenes, so that no judgment could be formed until one knew which paraffins or which olefines were present.

It may be urged that the quantitative classification into groups is the necessary first stage, but the question is whether there is any value in a knowledge of the first stage if the second stage, namely, individual subdivision of the "group" is, as far as we can judge, impracticable.

On the other hand, a simple, rapid and direct test with an experimental engine will give precise information on the motor value of the spirit which, we have the strongest reason to believe, cannot be calculated in view of the insuperable difficulty of determining the amount and constitution of each individual component.

A method of analysis of a mineral which went so far as to prove that it contains a metal in Group II. but held no prospect whatever of deciding if the metal is copper, gold, tin, cadmium, platinum, mercury or arsenic, would be of no use to the metallurgist.

Mr. G. R. Nixon said that one thing he would like to ask Dr. Garner was as to the utility of the iodine method in routine work. One was dealing with a cracked spirit; one had a cracking still which was normally standardised, and when one's unrefined cracked spirit was obtained it was normally refined by sulphuric acid treatment or by vapour-phase treatment, and the ordinary test, such as distillation and density, and original tests when the plant was first standardised, were quite sufficient to run a check on the gasoline without going to the extent of the lecturer's complicated analysis. He did not know what other use the iodine value method would be except for research.

Dr. Garner stated that cracked spirits with 50 per cent. olefine content could only be obtained from vapour-phase cracking. That was inaccurate because there were some paraffin waxes which gave gasolines of 50 per cent. olefine content on low-pressure cracking at a temperature of about 420° C., and they in some cases reacted very violently with 90 per cent. acid at ordinary temperature.

Coming to the nitric acid treatment of cracked spirit, he did not know whether the lecturer had tested out the Egloff and Morrell method. It was only a very approximate method, but in that method in using the nitrating mixture—which was a mixture of 25 per cent. nitric acid, 58 per cent. sulphuric acid and 17 per cent. of water, it was extremely difficult to wash out of the spirit, after nitric acid treatment, nitro bodies. They could not be got out very easily with further quantities of other nitrating mixture or nitric acid; there was always a pale yellow colour left in the spirit, which could not be got out either with water or soda. In fact the action with soda was interesting. It was a kind of pseudo-body which was dissolved, because when one washed the spirit

with soda the pale yellow colour changed to an orange red. The colour was also shown in the soda too, but prolonged washing of the spirit with soda did not take it out completely. That so-called pseudo nitro body was soluble in aniline, because when an aniline point test was done on the spirit the yellow colour disappeared immediately. He would like to ask Dr. Garner if he got the same reaction with fuming nitric acid even at the low temperature of 10° C. because that certainly would vitiate his aniline test.

Coming to refining by sulphuric acid—the question of polymerisation—every one knew that a cracked spirit gave a certain amount of polymers when treated with commercial quantities of sulphuric acid, and it was usual to take those polymers out by steam distillation up to the original end point. When a cracked spirit was exhaustively treated with sulphuric acid, Dr. Garner stated that a certain amount of naphthenes and paraffins were attacked, but he (Mr. Nixon) and Mr. Minchin had found that at low temperatures no reaction took place with the naphthenes and paraffins ; only polymerisation of the olefines took place, and that one could get those polymerised heavy bodies, such as Dr. Ormandy had described in his papers, separated by a normal fire or steam distillation. One could take the aniline point of the distillate after this steam or fire distillation, which was actually the aniline point representing a certain mixture of paraffins and naphthenes, and was not depressed or raised by the presence of polymerised bodies.

Coming to the solid trinitro compounds in Dr. Garner's nitric acid treatment, did Dr. Garner find in his nitric acid treatment those solid nitro compounds at the inter-surface of the nitric acid and the gasoline ; because if they were present in any reasonable quantity they might occlude some of the gasoline. Did he get a clean separation ? In the Egloff and Morrell method one did get that sometimes happening, and it was a source of trouble and error.

With regard to the gasoline from the cracking of paraffin wax which Dr. Garner refined he would like to ask Dr. Garner what method he had used to refine that gasoline.

Dr. Garner had cracked the residue from the gasoline ex paraffin wax in which he had obtained a gasoline containing olefines 47 per cent., aromatics 1 per cent., naphthenes 10.5, and paraffins 42. He would like to know the conditions of cracking of that residue. He was surprised to see that 10.5 per cent. of naphthenes, unless it was a very high-pressure crack.

Mr. R. Pitkethly thought Dr. Garner's paper was the type of paper which the members of the Institution required in order to stimulate their minds. The subject was intensely interesting to petroleum technologists, and particularly to those who were

interested in the products of cracking, as a reliable method of analysis would be of great value in their work.

Most of the points he had meant to refer to had already been mentioned, but there was one question he would like to ask, namely, had any attempt been made by the author to correlate the results of analysis by his method with engine tests made on the blends of hydrocarbons which he had selected for his experiment, or on mixtures of comparatively pure compounds of the different series of hydrocarbons?

Dr. F. H. Garner, in reply, said: The quotation of Dr. Ormandy's from the German philosopher that "If you want to study systems of philosophy, devote nine-tenths of your time to reading the first two chapters," is, of course, fundamentally sound, but in view of Dr. Ormandy's opening remarks, it would appear that he has not been able to apply this system to the present paper.

The method of analysis given was not put forward as a method of evaluating petrols as regards their behaviour in the internal combustion engine.

It is generally recognised that for the rating of motor fuels, chemical analysis of the fuel is a very indirect method of procedure, as engine tests can be made very quickly and give fairly accurate comparative values in a very short time.

A few years ago analyses of motor spirits were made for the content of paraffin, naphthene and aromatic hydrocarbons and the toluene value, calculated from the analytical results, was taken to represent the relative value of the spirits in internal combustion engines. Such methods of analysis are given in the British Standard Specifications for Aviation Spirit (B.E.S.A. No. 121, 1923).

At the present time the view perhaps more generally held is that stated by Dr. Thole in his discussion of the paper: that the paraffin content of one spirit is composed of entirely different groups of hydrocarbons from those present in another spirit, and thus, that in general, the chemical analysis of the fuel bears no definite relation to the engine performance.

As stated in the introduction to the present paper, the method of analysis given is suggested as a preliminary step towards deciding whether there is any relationship between chemical analysis and engine performance—whether the latter view may not be equally as extreme as that accepted a few years ago. It is nowhere suggested in the present paper that any method of chemical analysis is suitable as a method of rating motor fuels in regard to their behaviour in internal combustion engines, but rather that engine tests may be used to determine the relative values of the various types of hydrocarbons present in gasolines if the chemical composition is known.

The analytical evidence available that the type of paraffin hydrocarbons in one motor spirit is entirely different from that present in another motor spirit is not very definite, and accordingly the second stage mentioned by Dr. Thole, that is separation of the metals of group 2, may not be essential.

Quite apart from the engine side of this question, as pointed out by Mr. Moore and Mr. Pitkethley, until the chemical composition of spirits produced by cracking is known, it will not be possible to elucidate the mechanism of the cracking reaction, and it is on such fundamental knowledge that future developments in the production of spirits of high anti-knock qualities depend to a large extent.

The value of the iodine number for routine work lies very largely in the short length of time necessary for this determination and the ease with which accurate results can be obtained. The method described in the paper is, as stated, based on the work of Faragher, Gruse and Garner on the Hanus solution, and it is hoped that the details of the method given may be of some assistance in obtaining consistent results. The iodine number also furnishes a very rapid method of deciding whether cracking is being carried on uniformly; it is further of great value in following the various stages of chemical refining in order to decide whether the acid treatment is being carried out satisfactorily, both with a view to economy of acid and to the reduction of loss of olefines in the treatment.

The use of refractive indices as a help towards a solution of the problem was tried in the early stages of the present research and also of refractive dispersion, using the yellow, green and violet lines from a mercury vapour lamp, but was abandoned for the following reasons:

1. The data on refractive indices which are available for hydrocarbons, and particularly for olefines, are not very reliable.

2. The refractive indices appear to follow very closely on specific gravity, and thus very little more can be deduced from the refractive index than is already available from specific gravity figures.

On the other hand it is not difficult to obtain water-free aniline which will give consistent and accurate results in aniline point determinations.

Dr. Ormandy states that the high boiling material produced by the action of sulphuric acid on olefines are not polymers but are really open chain paraffins. In a recent paper in the Journal of the American Chemical Society, 1927, 49, 873, J. F. Norris and J. M. Joubert state that by the action of sulphuric acid—whether concentrated or dilute—on the various isomers of amylene, is one of polymerisation—dilute acid giving dimers, and strong acid higher polymers. Ten parts of trimethylethylene mixed with one part concentrated acid gave mostly the dimer.

The accuracy of the method for the estimation of paraffins and naphthenes in the cracked spirits depends on the fact that nitric acid under the same conditions, as used for the separation of olefines and aromatics, does not act upon the paraffins or upon the naphthenes or upon both, to any appreciable extent.

One of the first " premises " examined was naturally the action of nitric acid (under the conditions of test) on spirits of high naphthene content. Straight-run spirits, including Californian spirit, have been analysed by the nitric acid method dealt with in the present paper, and the aniline point of the product corresponds very closely indeed with that obtained by the I.P.T. method. Thus the error in this part of the method is comparable with that of the I.P.T. method.

It should perhaps be made clear that the present method of analysis utilising nitric acid is only suggested for use where olefines are present, as the I.P.T. method is much simpler for straight-run spirits. But the method for the determination of paraffins and naphthenes in spirit after acid treatment is, of course, equally applicable to straight run and cracked spirits, whether nitric acid or sulphuric acid is used to effect the separation of the paraffin and naphthene hydrocarbons.

The spirit after the nitric acid treatment is of pleasant odour and no nitro-compounds are introduced into the spirit as is the case with the Egloff-Morell method. No solid nitro-compounds have up to the present been found at the interface of gasoline and nitric acid, even with gasolines of high benzol content.

The method of analysis given is suitable for the analysis of cracked spirits as marketed, and is not recommended for unrefined spirits of the type produced in the early days of cracking.

Mr. Moore raises the question of the composition of the cracked spirit. A cracked spirit derived entirely by cracking a heavy residue often contains around 50 per cent. olefines and 50 per cent. saturateds, as is the case with the paraffin wax in the present paper. The percentage of unsaturated to paraffin varies to some extent from the 50 : 50 ratio according to the conditions of cracking. The highest percentage of olefines the author has come across in this connection is the spirit F.7, which was a very light aviation spirit, produced by the Lodge-Tinker vapour phase process, the content of olefines being over 85 per cent. The results of engine tests on this fuel made by E. G. Ritchie are reported in the report of the Advisory Committee for Aeronautics I.C.E. 281 (1919). Calorific Value R.A.E. H.C. Report 410 (J. Inst. Petr. Techn. 1921, 1, 339).

The action of sulphuric acid and nitric acid on a cracked or straight-run spirit depends very largely on the conditions of mixing,

but in the method given in the I.P.T. method, as modified, the naphthene hydrocarbons are not attacked to any appreciable extent. On the other hand it has been shown in Engler's Laboratory by Sentke (Engler, Das Erdol, 1, 234) that even normal heptane and octane can be sulphonated at ordinary temperatures by agitation with concentrated sulphuric acid. Normal octane can be completely dissolved by shaking with further quantities of sulphuric acid.

In reference to the question asked by Mr. Nixon, the method of refining the gasoline produced by cracking the paraffin wax was as follows:

1. Treatment with ½ per cent. of 80 per cent. sulphuric acid, followed by the usual neutralisation.

2. Distillation through a suitable fractionating column until the petrol has the required percentage over at 100°C. The cracking of the paraffin wax was made at approximately 200 lb. per sq. in. only.

It seems reasonable to expect that, if naphthenes are produced in small amounts by the first cracking of paraffin wax, the residue also will contain naphthenes, and examination of the residue shows that some oily matter is present as it does not crystallize sharply. On cracking this residue the naphthenes will probably give rise to a higher percentage of naphthenes than was present in the spirit produced by the original cracking of the paraffin-wax.

The main difficulty in producing mixture of synthetic hydrocarbons in order to test out such a method as that proposed in the present paper is that a number of each type of hydrocarbons—olefines, aromatics, naphthenes and paraffins—must be used. A mixture of amylene, benzene, cyclohexane and octane, for example, is useless for this purpose, where it is assumed that the olefines present are uniformly distributed over the whole distillation range. It was on account of the difficulties of obtaining at least three of each group of hydrocarbons in a pure state that the indirect method given in pages 709 to 712 was adopted.

The President said it was quite evident from the discussion that chemists did not agree on this very difficult question. He supposed they must congratulate themselves that that was so, because, generally speaking, if all chemists agreed with one another not very much progress would be made. Somebody was going to get to a correct solution some day, however much disagreement there was on the matter at present. They might comfort themselves with that thought.

The members had listened to a very excellent paper from Dr. Garner. It was a narration of a vast amount of study, and he was sure the members would wish him to convey to Dr. Garner the Institution's best thanks.

The meeting then terminated.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

RUMANIAN BRANCH.

The ELEVENTH GENERAL MEETING of the Rumanian Branch of the Institution of Petroleum Technologists was held at the Industrial Internationale Club, Ploesti, on Friday, February 3rd, 1928, the chair being taken by Mr. T. P. Perrott.

A paper was read upon

Efficiency of Back-Pressure Methods in Meotic Wells of Rumania.

By J. L. CHAILLET (Member),

of which the following is a précis :—

Back-pressure is only part of the problem of gas preservation and waste of gas means waste of possible oil. Statistics prove that the ultimate production from a well under back-pressure is considerably larger than without, and at the same time the quantity of sand brought out with the oil is reduced to a desired limit.

Back-pressure involves a reduction in expansion, due to flow-bean and separator, tubing, and casing perforations. These influence rate of oil flow, gas-oil ratio, pressure in tubing, temperature of oil at outflow and in tubing, and waxing-up.

The Meotic oil-sand of Moreni is very fine grained, 99·5 per cent. passing 150 mesh, and special care is necessary. An hourly measurement of sand percentage is advisable. A sudden increase of opening, even of three seconds, as when changing flow-lines, may change sand percentage from 0·1 to 0·4 per cent., the disturbance lasting 2 to 3 hours.

General practice in Rumania is to use shop-perforated casing with $\frac{3}{4}$-inch or larger holes. These holes are too large.

At the start of production the sand yielded should not exceed 0·5 per cent., being reduced to 0.2 per cent. after about a fortnight.

The setting-point of the wax in the oil from the first Meotic sand is 23°, therefore the oil should be received at a higher temperature than this to prevent waxing-up.

A gas-oil ratio of over 1000 cub. m. gas per 1 cub. m. oil is prohibitive.

An analysis of oil from one well was highly in favour of back-pressure. When pumping, the percentage of benzine was 21, when bailing 11 to 18, and when swabbing 6 to 11. Water production also decreased considerably when pumping.

A discussion followed and the meeting concluded with a vote of thanks to the author.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

TRINIDAD BRANCH.

THE FIRST GENERAL MEETING of the Trinidad Branch of the Institution of Petroleum Technologists was held at the office of the Apex (Trinidad) Oilfields Ltd., on Wednesday, February 29th, 1928.

Mr. A. Frank Dabell, M.I.Mech.E., Chairman, presided.

A paper was read upon

Coring Practice.

By G. H. SCOTT, B.Sc. (Associate Member).

of which the following is a précis :

The author roughly sketched the development of the modern core drill, showing how it had been adapted for use in the oil industry from the diamond and Calyx drills as used for prospecting for oil and other minerals.

He showed how the demand for accurate formation samples in rotary drilling had led to the evolution of barrels of the present type which, as they were designed to take cores of 20 ft. and upwards, allowed of continuous coring with high percentage recoveries, and that the main improvements of late had been in the design of the core head and core catchers. The use of stoodite and stellite, and more recently barium insets, had greatly increased the life of the core barrel cutting head, while recoveries had been increased by careful design of the core retainer.

He gave the general precautions to be adopted when taking a core, stressing the danger of burning the core if the speed of rotation was too high, and pointed out that most manufacturers recommended a figure of 35 r.p.m. In order to facilitate the correct limits of the depths of a core, if a portion of the core is dropped he recommended that the driller should keep a careful check of the depth of any change of formation noted when taking the core.

The examination of the cores should be made as soon as possible

after extraction, as they then often exhibit characteristics of colour, oil saturation and the presence of gas which may not be observed later. The percentage extraction should always be noted, together with the type of barrel used, as this gives a means of comparison of the efficiency of any type of barrel for a given type of formation. If the extraction is low, the limiting depths of the portion recovered can often be determined by reference to the driller's log.

In the examination of the core it should be split vertically, as in this way only can a correct description of the formation be made. The description should include dip and the main lithologic characters, together with the type of bedding, signs of slickensiding or contortion and any fossil or foraminiferal content. In the case of sands, watered sands are generally of a grey to greenish colour, and as most underground oilfield waters are characterised by high sodium chloride contents, the presence of water in any sand can usually be detected by washing the sand with an equal volume of distilled water and carrying out a simple titration with silver nitrate, using potassium chromate as indicator. With regard to oilsands, he stressed the fact that it is almost impossible to forecast the degree of saturation when the sands are loose and unconsolidated, as there is always a danger of the circulating fluid washing the sand to varying extents. The type of oil, however, can be determined by a Soxhlet extraction apparatus evaporating to dryness, and examining the residue for paraffins and naphthenes.

If screen pipe is to be used, a screen test on the cored sand sample will yield valuable data as to the size of mesh of screen that is most suitable.

He concluded by giving a list of the main uses of coring, which included :—

1. The location of a marker bed.
2. The location of suitable casing seats.
3. The location of oilsands, especially in deep wells where the head of fluid in the hole is liable to hold back the gas and oil.
4. The location of water sands.
5. The correct spacing of screen or perforated casing when it is necessary to produce from a number of sands.
6. The preparation of complete and detailed logs by continuous coring in selected localities so that an idea of the trend of deposition can be obtained. This is very important in areas characterised by lenticular deposits.

A discussion followed, and the meeting terminated by a vote of thanks being tendered the author, and the directorate of the Apex Company for the use of the room.

Surveys of New Oil Countries.*

By C. S. Cleverly (Associate Member).

Accurate surveys of a country where oil drilling operations are in progress may be grouped under three headings: (1) Preliminary, from existing maps, for the location of refinery sites, etc.; (2) Detailed, in the country where the field is located, and (3) Final where drilling operations are successful, to modify, if necessary, schemes prepared from the previous surveys.

The Preliminary Survey results in a map showing approximate locations for refinery, pipe-line route and pumping stations, storage depots, etc., and the Detailed Survey should provide sufficient information for the preparation of practical schemes and accurate estimates for the refining and distribution of the oil. The schemes prepared must be far-sighted and capable of economical extension at a later date.

In selecting sites for refineries, storage depots, etc., due regard must be paid to existing waterways, railways and roads, and information must be obtained regarding facilities for handling large and heavy machinery and plant, and particulars of freight rates should be obtained.

Water supply is of great importance, especially for the refinery, and should receive particular attention.

The ability to obtain building and other materials locally is of importance, and the question of utilising local labour for constructional work should be investigated.

The advantages of undertaking a thorough survey while drilling operations are in progress amply repay the expense. Sufficient information is obtained to formulate a policy to deal with a large or a small yield of oil and hasty decisions, made through lack of accurate knowledge, are avoided.

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* Precis of paper read before the Persian Branch of the Institution of Petroleum Technologists.

Some Present and Future Aspects of Petroleum Chemistry.*

By Benjamin T. Brooks, Ph.D., F.C.S. (Member).

The present discussion is not intended to be a compilation or an abstract of what is known regarding the chemistry of petroleum hydrocarbons. This has recently been very well summarized by Burrell.[1] An attempt will be made, however, to indicate some of the research problems along the fringe of our knowledge and some of the subjects that are engaging the attention of investigators in the general field of petroleum chemistry. Both theoretical and industrial subjects are considered.

The Relation of Research and Engineering in the Present Petroleum Industry.

A recent statistical survey published by the *Oil and Gas Journal* shows that the average American petroleum refinery represents a plant investment of about $5,000,000; of this amount $10,000 represents the laboratory. This is a fact worth examining closer. Those who apparently think that the world owes all research chemists a living could possibly make a great deal of capital out of this fact. But I believe a close examination of the situation will not be to the discredit of the industry. Other pertinent facts are as follows:—

The American petroleum industry is directed by men who are as quickly appreciative of research as other American industries. But the last ten years has witnessed a feverish improvement of most refineries, improvements which may be fairly characterized as engineering rather than chemical. The urgent problems have had to do with the production of the major products of the refinery, twelve billion gallons of gasoline, half a million tons of petroleum asphalt, and the increased production of lubricants demanded by our twenty-two million motor cars. A couple of years ago, Mr. Walter Miller estimated that the increased values and savings effected by American refineries solely by the adoption of improved methods of fractionation amounted to at least $120,000,000

* Paper received October 5th, 1928.
Ind. Eng. Chem., 1928, **20**, 602.

annually. To this we must add the value of many millions of barrels of crude oil saved by the study of crude oil emulsions ; half a million barrels of emulsified crude are treated by one well-known process. The gaoline now recovered from natural gas and refinery still gases is now well over one and one-half billion gallons annually.[2] The loss occasioned by treating cracked gasolines high in sulphur has been estimated at about $50,000,000, but the method of refining at low temperatures worked out by Halloran makes possible the saving of the greater part of this loss. Vapour-phase refining of cracked gasoline by Fuller's earth is distinctly more economical than the acid method commonly used. The use of high vacuum made possible by modern welding methods enables the refiner to obtain much greater yields of lubricating oil, and of better quality ; Howard and Loomis[3] state that a typical Mid-Continent crude yielding 6 to 7 per cent. of lubricating oil by the older common method, yielded 24 per cent. of lubricating oil of the same viscosity by the use of a high vacuum pipe still. Much steam and fuel has been saved by the increasing use of proper fractionating towers, avoiding the necessity of re-running, and much steam has also been saved by the use of high vacuum for the distillation of lubricating oils, just mentioned. Corrosion of refinery equipment has been considerably reduced, and considerable labour, as well as fuel and other charges, has been saved by the use of cracking, distillation and treating units of larger capacity and greater efficiency and the use of automatic heat control devices, the improvement of furnaces and the saving of heat by the use of radiant heat, partial recirculation of hot flue gases in certain cases and the conservation of heat by proper insulation material, all represent an enormous annual saving. Peterkin states that whereas in old shell still practice a heat input of 32 per cent. was common practice, and anything over 50 per cent. a rare achievement, modern pipe still practice gives a heat input of 75 per cent. or better. All this represents an annual saving or increased values, for the American petroleum industry, of at least *half a billion dollars*. But, due to the competitive nature of the industry and the abundance of crude oil, most of this half billion dollars is not in the refiners' pockets, but has been passed on to the public. A refiner using the methods of 1918 could not survive.

The point about all this which bears upon the $10,000 laboratory mentioned above, is that very few of those improvements were ever worked out in the laboratory. Petroleum refining has developed a technology of its own, and most of the men who are responsible for this development, particularly the achievements of

[2] *Nat. Petr. News*, Dec. 14, 1927, 28.
[3] 1,356,800,000 gallons in 1926.

the last ten years, have been scientifically minded men, either chemists with some appreciation of engineering or engineers with some appreciation of chemistry, or "chemical engineers," if one prefers that term. One only has to mention a few well known names such as Burton, Midgely, Roy and Walter Cross, Burrell, T. T. Gray, Halloran, Dunstan, De Florez, Wilson, Stratford and W. K. Lewis to illustrate this point.

It is true that most of the improvements in refinery technology, which have been so hastily mentioned, have been the engineering applications of research which has been done somewhere. Refinery research is still very much concerned with getting better engineering data, the physical properties of crude oils and distillates, the physical properties of steels and alloys at high temperatures, special materials for resisting corrosion, etc. But the opinion is hazarded that the last ten years of rapid engineering improvement represents a phase, a very necessary phase in the development of the industry.

As long as there is a petroleum industry, it must produce much the same major products as it produces now, *i.e.*, motor fuel, lubricants, wax, petrolatum, and perhaps gas oil, kerosine, and asphalts. Research can hardly change the general aspect of the refining of petroleum, although it seems certain that the time is not far off when at least a considerable proportion of these products will be made from coal.

What are the signs for the future? Bearing in mind the expenditure of $10,000 for the average refinery laboratory, it will be noted that half a dozen of the largest refining companies have built and equipped research laboratories whose equipment and personnel would be a credit to any university campus. Any one could name many reasons for the bigness or the financial resources of these particular companies, but certainly not the least important of these reasons has been aggressive progress and foresight. The opinion of the directors of these large companies of the value of research has been tangibly expressed.

There is another significant fact. Many refiners are to-day seeking a greater diversity of products, believing that this will tend to stabilize the refining industry and enable them to get a greater net profit from a barrel of crude. So long as fuel oil must compete with coal, the profit, if any, must go to the producer. More careful consideration than ever before is now being given to the possibility of more diverse manufacture, and this resolves itself into chemical possibilities, which will be discussed further.

Still another reason for the interest of the refiner in research has been the somewhat threatening development in Europe of the processes for manufacturing motor fuel, waxes and lubricants from coal or from water gas. Considerable interest has been

aroused in these processes by their inclusion in the recent report of the Federal Oil Conservation Board, by the reported acquisition by the Standard Oil Co. of New Jersey of the American rights to the Bergius' process, and by the fact that the Bergius' process is actually operating on a commercial scale in Germany. The facts are that, operating on German soft coals, the Bergius' process yields 93 to 133 gallons of crude oil per ton of coal, of which crude about 40 gallons is suitable for use as motor fuel. Hydrogen is taken up by the powdered coal at operating temperatures of 800°–900° F. and 2100–3000 lb. pressure. One naturally compares it with modern cracking processes, employing approximately the same temperatures but at about one-tenth the pressure, single units putting through three thousand barrels or more of raw oil charging stock and producing 35 to 45 per cent. of gasoline. The investment and operating costs of the Bergius' process are certainly higher than for any of the modern oil cracking processes, and, while it is difficult to see how the Bergius' process can be operated at a profit in this country, as long as crude oil and gasoline are produced at anything like their present costs, it is reassuring as regards our future supply of motor fuel, and is a striking example for the oil industry of the method of research followed by skilful engineering. The possible menace from motor fuel made from water gas is probably not so serious. Smith, Davis and Reynolds[4] report that about 1400 cu. ft. of water gas was required to produce 1 gallon of liquid oil. At a cost of 20 cents per 1000 cubic feet of water gas this would mean a *material* cost of 28 cents per gallon. Fischer has reported yields which would correspond to a material cost of about 20 cents per gallon. Bergius has stated that one of the favourable developments in connection with his process is the production of hydrogen from methane through water gas. The mere fact that such researches may threaten the future of the entire petroleum industry is sufficient to cause anyone to consider the possibilities of research most carefully.

Coming back to the question of the average $10,000 laboratory, it must be noted that there is included in this average a large number of refineries that are poorly equipped, badly situated and which certainly will not survive. Pogue, in his statistical study, "The Economics of Petroleum," states: "Small incomplete refineries spring up in proximity to flush production only to die again as the wave of oil field development passes on. . . ." "Refinery capacity is considerably greater than the needs of the country; that much of this capacity is poorly located for survival that a notable percentage of the capacity is of the skimming or

[4] *Ind. Eng. Chem.*, 1927, **19**, 801; 1928, **20**, 462.

incomplete type, and hence poorly adapted for profitable operation with high cost crudes. . . . Projected into the future, these conditions spell considerable readjustment in the refinery situation." The manufacture of a still greater number of finished products than are now made by the complete refinery is a further development of the idea expressed by Pogue. As recently as 1899, 60 per cent. of the value of an average barrel of crude was represented by kerosine.

Technical developments and research have very much affected the basic cost figure of the petroleum industry—*i.e.*, the price scale of the various crudes. This is well worth noting, as the relative abundance of crude is by no means the only important factor. The outstanding importance of kerosine in 1899 has been mentioned. It is also well known how for many years following the development of the gasoline business the price scale of crudes was based primarily on gasoline content. As recently as March, 1926, the price differential per 1° Beaumé, taken roughly as an indication of the gasoline content, was 10 cents. In February, 1926, Mr. W. C. Teagle stated before the Federal Oil Conservation Board : "The price differential between gasoline and the fuel oil values of these fuel and high sulphur crudes was the incentive for the further development of cracking processes which have been perfected within the past two or three years, and the industry from them." The price differential for each degree Beaumé or degree A. P. I. gravity is now about 3 cents. Only recently has the study of the anti-knock properties of different gasolines disclosed the fact that certain oils, such as the Mirando, Smackover, Spindle Top and certain California crudes, yield cracked gasolines of very superior anti-knock value. The use of tetra ethyl lead, vapour-phase gasoline, or benzol all add to the cost, so that if the price differentials for premium anti-knock motor fuels continues, this should be reflected in the crude price scales for these unusual oils. Another technical development which may affect the relative price of these crudes which are substantially free from wax, is the distillation of lubricating oils under very high vacuum, already mentioned.

Present Trend of Petroleum Research.

Having indicated briefly the engineering advances in the refining branch of the industry, and some of the reasons for the growing importance of research, a few of the objectives of current research will be pointed out. Of course, much of the research being done is carried on privately, and little or nothing is known of it until eventual success brings it to light. But a few lines of current progress are well marked.

Having in mind mainly chemical investigations, it may be convenient first to consider natural gas and refinery gases. The value of natural gas as fuel in populated industrial areas makes it almost out of the question to consider its use for any other purpose. However, in many fields in the south and west, large quantities are still wasted or burned for carbon black. In 1926 there were produced about 187 million lb. of carbon black from about 130 billion cu. ft. of gas, or about 1·4 lb. of black per 1000 cu. ft. A new process is now in commercial operation producing about 9 lb. of carbon black per 1000 cu. ft., which may put carbon black manufacture on a more secure economic basis. In addition to this, much work has been done on the pyrolysis of natural gas, and also of the hydrocarbons other than methane.

One of the most interesting developments of industrial interest is the manufacture of benzol from natural gas. Gases comparatively rich in hydrocarbons other than methane give much better yields of benzol than those high in methane. Pure ethane yields about 25 per cent. of condensable products at 800–900° C. The cracking of butane is carried out industrially for the production of ethylene and propylene, which is used for the manufacture of somewhat more than 30 tons per day of the corresponding glycols and related compounds. The residual gases from these pyrolytic reactions are rich in hydrogen, but *cheap* natural gas is chiefly found in comparatively unpopulated areas usually in conjunction with flush oil production in new fields. Plant installations for its utilisation should therefore be such as can be moved after a few years or even abandoned without great loss. This and the presence of methane apparently precludes the use of such hydrogen for ammonia synthesis. Dunstan has pointed out that when steam is used in the benzol process, the residual gas contains hydrogen and carbon monoxide, and is accordingly capable of being converted catalytically into liquid hydrocarbons by the Fischer or Patart methods. Although few dependable analyses of natural gas have been made upon which an estimate might be made, the amount of ethane, propane and butane certainly exceeds the amount of recoverable gasoline in natural gas, probably, five fold. The operation of these two processes therefore offers the *possibility* of producing an excellent anti-knock motor fuel, in quantities about equal to the amount of natural gas gasoline now produced. However, if the larger scale development fulfils the promise of the experimental work, it is doubtful if the installation of the process would be possible on such a widespread scale as the recovery of gasoline now is.

The utilization of the ethylene, propylene and butenes in refinery gases from cracking operations is receiving greater attention.

However, only the larger cracking plants have sufficient quantities of such by-product gases to make their utilization attractive. With the use of higher cracking temperatures to obtain gasoline of good anti-knock value, and in some cases the manufacture of vapour-phrase gasoline,[5] entailing greater fixed gas production, the chemical utilization of the olefins in those gases is receiving greater attention. Since these gases are now valued only for their *fuel value* at the plant, it seems certain that the solvent alcohols, particularly pure secondary butyl and secondary amyl, will displace solvent alcohols from other sources to a large degree, since it has very recently been shown that these alcohols can be manufactured from these hydrocarbons in a very pure and commercially satisfactory condition.

The perfection of fractionating towers in the natural gas gasoline industry has shown that it is entirely feasible to produce the smiple saturated hydrocarbons in a practically pure condition, at low cost. Ethylene, propylene, butenes and amylenes contaminated only with the corresponding paraffins should therefore be available in quantity.

The work of Burrell on the analytical separation of the constituents of natural gas at low temperatures showed the very great differences in vapour pressure between methane, ethane, propane, and butane, at low temperatures, a fact also emphasized in a recent patent to W. K. Lewis.[6] One of the most promising methods of utilising these saturated and olefinic hydrocarbons is their partial oxidation to products of established commercial value. The commercial oxidation of natural gas (methane) to formaldehyde and methanol by the Empire Refining Company has greatly stimulated investigations along this line.

The slow oxidation of olefins at low temperatures probably indicated the mechanism of oxidation of such hydrocarbons in processes of partial combustion. At ordinary temperatures molecular oxygen combines with the double bond to form peroxides, as was first shown by the well-known work of Engler and Weissberg[7] in the case of amyene and hexylene, and by the writer in the case of cracked gasolines.[8] These peroxides break down to form alde-

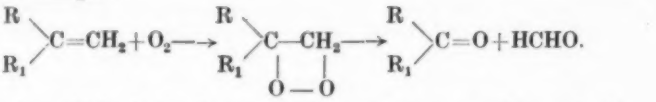
[5] Dunstan, *loc. cit.* notes that the gases from ordinary pressure cracking operations contain very little ethylene, but states that the composition of gas from vapour phase cracking is indicated by the following case : the gas contained 55·7 per cent. unsaturates of the following character, ethylene 54·0 per cent., propylene 28 per cent., butanes 9·0 per cent., amylenes 1·7 per cent., higher olefins 6·1 per cent., butadiens 1·2 per cent.

[6] U.S.P. 1,672,849 (1928).

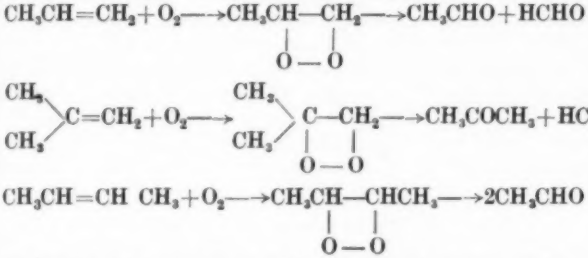
[7] Ber., 1900, **33**, 1094.

[8] *Ind. Eng. Chem.*, 1926, **18**, 1200.

hydes and ketones, according to the structure of the original olefin, as for example :—



Thus formaldehyde has frequently been noted among the products of air oxidation of the terpenes, and is very pronounced in the fore-runnings when cracked gasoline, oxidized by standing in contact with air, is distilled. If the same mechanism of oxidation holds at higher temperatures, propylene should give acetaldehyde and formaldehyde, isobutene should give acetone and formaldehyde, butene-2 should give acetaldehyde, as follows :—



Of course other reactions take place, carbon monoxide, carbon dioxide and water always being formed. The investigations of Wheeler and Blair[9] on the oxidation of methane and ethylene to formaldehyde are of particular interest and they interpret their results by the hydroxylation theory of oxidation of Bone and his co-workers. Thus Wheeler and Blair obtained high yields of acetaldehyde, which they regard as being formed by the hydroxylation of ethlene to vinyl alcohol and the rearrangement of the latter to acetaldehyde. The investigation of the detonation of motor fuels, or rather engine knock, has led to thorough investigation of the chemical mechanism of hydrocarbon combustion, which investigation is in progress in several research laboratories. These investigations have already thrown considerable doubt on the hydroxylation theory, and Callendar[10] finds evidence of the formation of peroxides and notes that "incipient oxidation" occurs at lower temperatures with motor fuels which knock than with non-knocking fuels. Pease and Chesebro[11] state that in the oxidation of propane and butanes the reaction may start abruptly

[9] *J. Soc. Chem. Ind.*, 1922, **41**, 303T ; 1923, **42**, 260, 263.
[10] *Engineering*, 1927, 123, 147, 182, 210.
[11] Paper communicated at the St. Louis meeting, Am. Chem. Soc., 1928.

at temperatures as low as 300° C., and that local over-heating may really be molecular. The importance of temperature control in the catalytic oxidation of benzene and naphthalene has been shown by Weiss and Downs[12] and the value of inert gases as diluents is made use of in the catalytic oxidation of methanol to formaldehyde. It is probable that the large excess of methane in the Empire Refining Company's process of methane oxidation may serve such a purpose, *i.e.*, temperature control. The whole subject is being actively investigated in many quarters.

In this connection it should be remembered that the oxidation of petroleum residuums by air as in the manufacture of air blown asphalts, takes place with amazing ease at comparatively low temperatures. The oxidation of paraffin wax at relatively low temperatures has been under investigation for several years and the manufacture of fatty acids suitable for soap stocks and wax-like esters in this way appears to be a possibility. The catalytic oxidation of petroleum vapours, in the presence of molybdic oxide, has been studied by J. H. James, who is now manufacturing an acrid mixture now being used as an alcohol denaturant. The Penniman process is also one of air oxidation but details of the process and the nature of the products has not yet been made public.

Polymerization.

The subject of polymerization is probably of more theoretical interest than of industrial importance, but the story of the synthetic resins suggests that equally important industrial results may come out of a study of the polymerization of hydrocarbons. Selective polymerization of the di-olefins mainly responsible for gum formation in cracked gasolines, is carried out in the Gray process of refining in the vapour phase by Fuller's earth, and sulphuric acid is also employed for the same purpose in the case of cracked distillates. Brownlee suggested the manufacture of low cold test, wax free lubricants by polymerizing unsaturated hydrocarbons by means of anhydrous aluminum chloride. The use of the silent electrical discharge is stated to be the basis of the " Voltol " process, operated in Europe, for increasing the viscosity of lubricating oils, and Lind has recently shown that the simple gaseous hydrocarbons can be condensed by this means, and by alpha radiation, to liquid oils. Although Lind points out that the consumption of electrical energy is apparently much too great for this process to become of industrial importance, it is of great interest as bearing on the mechanism of hydrocarbon polymerization.

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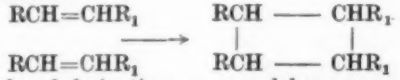
[12] *J. Soc. Chem. Ind.*, 1926, **45**, 188T.

It should also be noted that polymerization is the only rational explanation of the presence in crude petroleums of the hydrocarbons of high molecular weight which we value as lubricants. If we are to account for petroleums by their formation from the fatty residues of either animal or vegetable organisms, probably by anærobic fermentation, we cannot account for hydrocarbons of more than about twenty-two carbon atoms, except by polymerization. Petroleum-like products have been made from fatty acids by a variety of laboratory processes. But there never has been any evidence that oil bearing sedimentaries furnished the conditions of these laboratory processes, i.e., destructive distillation, heating with anhydrous aluminum chloride, radium emanation, etc. One might as well propose a Grignard synthesis to account for petroleum. The presence of cyclic hydrocarbons in petroleum is also to be accounted for in the same way since fatty acids in nature having cyclic hydrocarbon structures are exceedingly rare, as, for example, the chaulmoogric and hydnocarpic acids recently investigated by Adams. On the other hand, we now know of a fairly large number of cases in which polymerization yields dimers having cyclobutane and cyclohexane structures.

It is somewhat difficult to give a good scientific definition of polymerization, but in general terms it is the combination of two or more similar molecules without the formation of any other reaction product. In the case of hydrocarbon polymers, the original hydrocarbons are not easily regenerated, and then only in very poor yields. The whole subject cannot be reviewed here in detail, but the mechanism of polymerization is not the complete mystery that it is commonly supposed to be. The reason for the persistent obscurity and lack of understanding of the mechanism of polymerization probably lies in the deep rooted idea of the tetra-valence of carbon and the reluctance to perceive the behaviour of carbon in the bivalent and trivalent condition. The early work of Nef on bivalent carbon, Gomberg on trivalent carbon and the more recent work on free radicals makes possible a much clearer understanding of hydrocarbon polymerization.

Lebedev[13] distinguished four general types of polymerization :—

(1) The stilbene type ⟶ dimers probably having cyclobutane structure. Many dimers have since been shown to be cyclobutanes.



(2) Divinyl and derivatives ⟶ cyclohexanes and polymers of uncertain structure.

[13] *Chem. Zentr.*, 1912 (1), 1440 ; 1914, (1), 1402.

(3) Acetylene and derivatives——→benzenes.

(4) Styrene type ——→ very high molecular weight polymers of unknown structure.

At least two more types, based upon the character of the final hydrocarbon polymer, should be added to Lebedev's types :—

(5) Ethylenes ——→ unsaturated acyclic polymers.

(6) Trivalent carbon derivatives ——→ saturated hydrocarbons.

The above classification based upon the nature of the polymers may be useful, but it is perhaps misleading in suggesting that there may be different mechanisms of polymerization. I believe that abundant evidence has accumulated to warrant the theory that all cases of hydrocarbon polymerization occur by the direct combination bivalent or trivalent carbon atoms, and all known methods of causing polymerization may readily be explained on this basis. This is much more probable and in harmony with our theory of chemical reaction in general than the old fashioned way of writing reactions. The recent work on the behaviour of free radicals has a direct bearing on polymerization, and is properly considered as such. The behaviour of triphenyl methyl and direct combination in such instances of trivalent carbon is well known. Kraus[14] and his co-workers have pointed out the closely analogous behaviour between sodium methyl, $NaCH_3$, sodium triphenyl methane, $NaC(Ph)_3$ and the tri-alkyl and tri-aryl derivatives of tin, germanium and silicon. Compounds of the type $NaMR_3$ are salts in the true sense of the word. Their solutions in liquid ammonia are highly ionized. Thus, when sodium trimethyl tin is treated with trimethyl tin bromide, sodium bromide is formed and the two trimethyl tin radicals combine to form *hexamethyl stanno-ethane*.

$(CH_3)_3SnNa + BrSn(CH_3)_3 \longrightarrow (CH_3)_3SnSn(CH_3)_3 + NaBr$

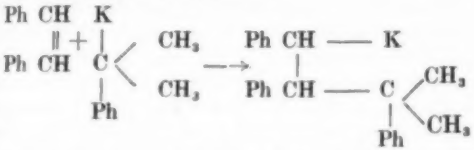
Hexamethyl stanno-ethane is readily decomposed by heating to trimethyl tin, which again "polymerizes," as Kraus says, completely to hexamethyl stanno-ethane.

The well-known Wurtz-Fittig synthesis of hydrocarbons is the same type of reaction, sodium alkyls and free radicals being formed, the latter combining directly. According to Schlubach and Goes[15] the Wurtz-Fittig synthesis exhibits the characteristics phenomena on which the hypothesis of the pre-existence of free radicals is based.

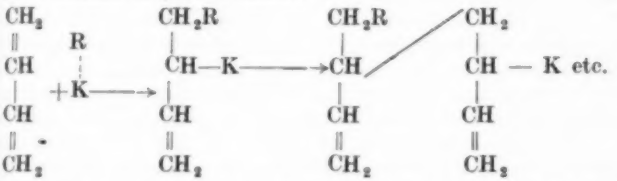
Closely related to the above reactions is the recent discovery of Ziegler and Bähri[16] that sodium alkyls may add to the ethylene bond. They were able to isolate the addition product, and show

[14] *J. Amer. Chem. Soc.*, 1925, **47**, 2361; 1926, **48**, 2131.
[15] *Ber.*, 1922, **55B**, 2889.
[16] *Ber.*, 1928, **61**, 253.

its constitution in the case of the potassium derivative of isopropyl benzol reacting with stilbene.



They have suggested that the repetition of such addition would explain the polymerization of the dienes by metallic sodium and be the sodium alkyls, as follows :—



The mechanism of the condensation of hydrocarbons by means of the silent electrical discharge and by alpha radiation is obscure. Demjanow and Prianishnikov[17] used the silent discharge to convert ethylene into a mobile unsaturated oil, and isobutene was converted mainly into the hydrocarbons C_8H_{24}. According to Bates and Taylor[18] the condensation of ethylene by excited mercury atoms is the result of a complex series of reactions, and they believe the initial reaction to be the elimination of *molecular hydrogen*, not atomic hydrogen. Splitting out atomic hydrogen and the formation of free radicals, they believe, is highly improbable on thermodynamic grounds. Lind and Glockler[19] have shown that the condensation of saturated hydrocarbons by alpha radiation and by the semi-corona discharge to liquid oils also occurs with the formation of hydrogen and methane. The oils formed are unsaturated, which would apparently agree with the suggestion of Bates and Taylor that they are not formed by the combination of free radicals. However, if molecular hydrogen is removed, as suggested by them, the residual hydrocarbon must initially have either a bivalent carbon atom or two trivalent carbon atoms in accordance with Nef's general theory of the dissociation of sulphuric acid or halogen acids from their hydrocarbon combinations, as will be discussed later.

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[17] *J. Amer. Chem. Soc.*, Abs. A., 1927, 336.
[18] *J. Amer. Chem. Soc.*, 1927, **49**, 2445.
[19] *Amer. Electrochem. Soc.*, 1927, **52**, 83.

In view of the fact that the electrical agencies just mentioned cause such a condensation, perhaps to be regarded as polymerization, of hydrocarbons, it is rather to be expected that ultra-violet light will cause polymerization. According to Plotnikov[20] vinyl chloride is rapidly polymerized in this way and Stobbe and Russ[21] showed that phenyl butadiene is more rapidly polymerized in the light than in the dark. Ethylene is converted into a mixture of liquid and solid hydrocarbons[22] and a recent inquiry by the writer shows that trimethyl ethylene and pentene-2 are also polymerized by this means. The reaction is probably a general one. Light also accelerates the polymerization of styrene and cinnamylidene acetophenone.[23]

The method of polymerization, which is probably of more interest in petroleum chemistry, is heat, or possibly heat and pressure. It is by no means certain that pressure influences polymerization. Cracking oil to gas under partial vacuum favours the production of a high yield of unsaturates, but rapid passage through the cracking zone produces substantially the same results.[24] The gasoline produced by vapour-phase cracking is much more highly unsaturated than that produced by distilling under pressure, but it is still possible that the difference is caused by polymerization of the unsaturated hydrocarbons, first formed, during the longer exposure to heat in the pressure processes. Where the volume change is considerable the principal of Le Chatelier would of course favour polymerization with increase of pressure. Polymerization is induced by finely porous absorbents such as Fuller's earth. There is some evidence that the improvement in colour effected by slow distillation of highly cracked gasolines through fractionating towers under moderate pressures is in part due to polymerization.[25]

It appears that under the influence of heat the stressed condition of the double bond is overcome, one of the electron pairs shared by the carbon atoms becoming available for more stabil combination. In other words two of the carbon atoms become momentarily trivalent. According to this view the dimers resulting from such change, in the case of simple olefins, should be first cyclobutanes. A large number of the dimers formed by the influence of heat are now known to be cyclobutanes. This has been shown by Lebedev[26] to be the case with the dimers of unsymmetrical dimethyl and trimethyl allene, and symmetrical dimethyl allene. The fact

[20] *J. Chem. Soc.*, 1922 (1), 419.
[21] *Ber.*, 1912, **45**, 3496.
[22] Berthelot und Gaudeschon, *Compt. rend.*, **155**, 521.
[23] Dziewonski and Rapalski, *Ber.*, 1912, **45**, 249.
[24] Whitaker and Alexander, *Ind. Eng. Chem.* 1915, **7**, 484.
[25] Brooks, *Ind. Eng. Chem.* 1926, **18**, 1208.
[26] *loc. cit.*

is sufficiently important to note other similar instances. Thus, according to Staudinger[27], the dimeric ketenes are 1·3-cyclobutanones, which conclusion is supported by the work of Dieckmann and Wittman[28] and by the absorption spectra of these substances investigated by Lardy.[29] Other examples are the conversion of cinnamic acid to the truxillic acids, the polymerization of unsymmetrical diphenyl ethylene to tetra phenyl cyclobutane, and the dimers of the following: dibenzal acetone, methylene malonic acid, dicarboxyglutaric ester, cinnamylidene malonic acid, cinnamylidene benzalcyanide, cinnamylidene acetophenone, cinnamylidene acetyl acetone, alpha methyl cinnamylidene acetic acid, styryl methyl ketones, the dimer of cyclopentadiene, etc. The list of such cyclobutanes could be considerably extended.

With the conjugated dienes the more stabil *six carbon ring* is possible and many examples of this type are known, as for example the polymerization of isoprene to dipentene and 1·3-dimethyl-3-ethenyl cyclohexene (6), the conversion of 2·3-dimethyl butadiene on heating to 150° to 4·6-dimethyl dipentene,[30] butadiene to 1-ethenyl-cyclohexene (3), etc. Closely related to the polymerizations just mentioned are the combinations of different unsaturated hydrocarbons, as for example the reaction of isoprene with *alpha* and *beta* phellandrene,[31] by heating together in sealed tubes, to new hydrocarbons ofthe sesquiterpene type $C_{15}H_{24}$.

Most of the polymerizations to cyclic structures have been caused by heat. It is possible that the formation of acyclic unsaturated polymers may in some cases take place through the intermediate formation of a cyclobutane ring which is then ruptured. The literature is very scanty regarding the stability of the cyclobutane ring to acids. In the case of *alpha* and *beta* pinene it is very readily broken, but in other cases it is not.

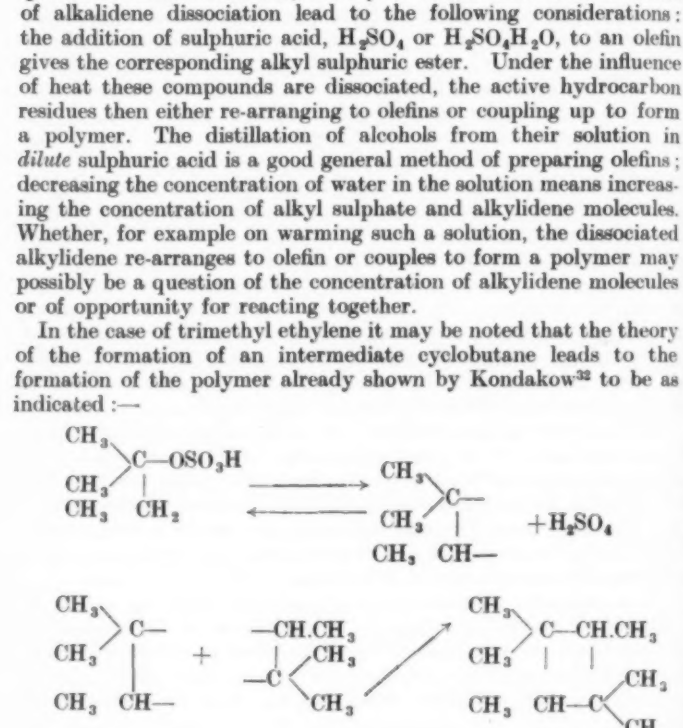
It is probable that all cases of polymerization by means of chemical reagents take place by the addition of the reagent to the double bond followed by the dissociation or decomposition of the addition product. There is evidence that finely porous absorbents, such as Fuller's earth, combine with the olefins which they polymerize, the decomposition of the combination giving hydrocarbon residues having at the moment trivalent or bivalent carbon atoms, just as in the case of other chemical reagents which are more easily recognized as such, as for example, sulphuric acid, zinc chloride, anhydrous aluminium and ferric chlorides, stannic chloride, etc. The evidence is that the dipolymers of trimethyl

[27] *Ber.*, 1920, **53**, 1085, *Helv. Chem. Acta.*, 1924 **7**, 3, 8.
[28] *Ber.*, 1922, **55B**, 3331.
[29] *J. Chem. Soc.*, 1925 (2) 88.
[30] Lebedev, *Chem Zentr.*, 1912, (1), 1440.
[31] Semmler, *Ber.*, 1914, **47**, 2080.

ethylene, formed by the action of Fuller's earth, are identical with those formed by sulphuric acid. It is possible that milder chemical methods of polymerization will yield cyclobutane dimers identical with those produced by heat.

Without going into detail and without discussing other antiquated or bizarre theories, it may be noted that Nef's theories of alkalidene dissociation lead to the following considerations: the addition of sulphuric acid, H_2SO_4 or $H_2SO_4H_2O$, to an olefin gives the corresponding alkyl sulphuric ester. Under the influence of heat these compounds are dissociated, the active hydrocarbon residues then either re-arranging to olefins or coupling up to form a polymer. The distillation of alcohols from their solution in *dilute* sulphuric acid is a good general method of preparing olefins; decreasing the concentration of water in the solution means increasing the concentration of alkyl sulphate and alkylidene molecules. Whether, for example on warming such a solution, the dissociated alkylidene re-arranges to olefin or couples to form a polymer may possibly be a question of the concentration of alkylidene molecules or of opportunity for reacting together.

In the case of trimethyl ethylene it may be noted that the theory of the formation of an intermediate cyclobutane leads to the formation of the polymer already shown by Kondakow[32] to be as indicated :—



[32] *J. pr. Chem.*, 1889, **54** (2), 455.

The trans-annular migration of a hydrogen atom as suggested is very similar to the many cases of such migration studied recently by Thorpe, Ingold and Kon. It will also be noted that the above balanced symmetrical ring leads to Kondakow's polymer, no matter where the rupture of the ring occurs. This polymer is the principal product, although two other dimers appear to be formed, being formed possibly from the unsymmetrical cyclobutane intermediate.

An olefine of the type RCH=CHR is very much more difficult to polymerize. The sulphuric esters are much more stabil. This type of sulphuric ester, or halogen derivative, dissociates according to Nef to give initially a residue having a bivalent carbon atom. The bivalent carbon atoms in such compounds should be much more reactive than the trivalent carbon atoms, and as a matter of fact it is very difficult to prepare the dimers of such olefins, the polymerization usually proceeding much further. It should be noted that in this type of olefin cyclobutanes cannot be expected as a result of acid polymerisation. Thus the dimer of cyclohexene should be, barring re-arrangement, di-cyclohexylidene.

Synthetic Rubber.

The question of polymerization is inseparably connected with that of synthetic rubber; petroleum continues to be considered by some as the most promising material for its successful manufacture. This idea is probably founded on the general idea that rubber is a hydrocarbon worth perhaps 50 cents. per lb., and petroleum is a mixture of hydrocarbons worth, in the form of gas oil, about ½ a cent. per lb. The difficulties, from the standpoint of the rubber chemist, are fully discussed by L. E. Weber,[33] who in the light of the research on the subject during the last twenty-five years is not very optimistic as to commercial production of satisfactory rubber. Viewed from the standpoint of petroleum, it may be said at once that it would not be difficult to produce an exhibition sample of synthetic rubber made from petroleum. As pointed out by Weber, it would probably be inferior to natural rubber, but it would certainly be good enough for industrial use if produced at sufficiently low cost. We now have had some sixteen years widespread study of petroleum cracking and considerable information of value from much earlier work. The whole teaching of all that is known about the cracking of oil is that when petroleum oils are cracked to produce appreciable quantities of dienes, such as butadiene, the variety and proportion of the other products is so large that the commercial utility of such a process would certainly be dependent upon the profitable utilisation of these major products, and the comparatively incidental extraction and purification of butadiene, isoprene and the like by methods yet to

[33] *Ind. Eng. Chem.*, 1926, **18**, 404.

be developed. Engler and Staudinger[34] indeed patented a process for the production of butadiene and isoprene by the cracking of petroleum in 1912, in the early days of the serious effort to produce synthetic rubber. Birch[35] has shown that the preparation of butadiene tetra-bromide from the "low boiling fractions of the liquid obtained by compressing oil gas or Pintsch gas," is not difficult, but the yields obtained are significant. Eight gallons of the low boiling hydrocarbon fraction yielded about 800 gal. of butadiene tetra-bromide, or about 14 grams of butadiene per gallon. The proportion of the original barrel of oil represented by the light hydrocarbon fraction is not given, but allowing 1 gallon for this light fraction, some idea of the yield of butadiene in this instance is obtained. A study of the problem must obviously include: (1) investigation to obtain the maximum yields of butadiene and isoprene; (2) methods for the separation and purification of the dienes; (3) methods for the best utilisation of the many other products formed. In this connection it is of interest to note that the interest of the Carbide and Carbon Chemical Company in ethylene glycol grew out of an attempt to manufacture acetylene by cracking oil at high temperatures, a considerable proportion of ethylene being produced along with the acetylene.

The commercial production of butadiene and isoprene from petroleum still involves a great deal of research, and its success certainly is interdependent upon a manifold utilisation of other products. By way of illustration a process for the oxidation of ethane to formaldehyde, patented by the Carbide and Carbon Chemical Company[36] may be given as an illustration. By partial oxidation at 700–710° C. the conversion of the ethane was as follows:—

Carbon dioxide		1·2%
Carbon monoxide and hydrogen ..	10·5%	
Methane	1·2%	
		11·7%
Ethylene	33·4%	
Aldehydes	7·4%	
		40·8%
Unchanged ethane		46·3%
		100·0%

The development of processes for the utilisation of water gas, ethylene, propylene, the butenes, the crude benzol referred to

[34] G.P. 265,172, 1912.
[35] *Ind. Eng. Chem.*, 1928, **20**, 474.
[36] E.P. 238,938, 1925.

above in connection with natural gas and their inter-dependent operation might make the synthesis of rubber from petroleum possible. Some of the basic considerations are that the plantations now in existence produce sufficient rubber for the world's needs, and it can be so produced at a cost of about 25 c. per lb. In other words, synthetic rubber, so far an inferior product, would have to be produced at a cost of less than 25 c. per lb.

The Sulphur Problem.

A great deal of attention, or at least discussion, is being given the sulphur derivatives present in petroleum, particularly in the motor fuel fraction. The chemical investigation of these sulphur derivatives is certain to yield information of scientific interest. The sulphur problems in petroleum are chiefly of two types: (1) the elimination of sulphur derivatives from gasolines, and (2) the removal of sulphur compounds or their chemical neutralisation prior to or along with the distillation of the crude in order to minimise corrosion of refinery equipment. One does not get very far in discussing these problems with a refiner before one finds that the complaint is a loud one, but that the refiner cannot afford to pay more than a few cents. per barrel to remove or neutralise several pounds of sulphur. While hydrogen sulphide may be a nuisance and does corrode equipment to a certain extent, this corrosion can to a large degree be controlled, and it is difficult to conceive of any chemical method of handling the problem that is as cheap as decomposing the sulphur derivatives to hydrogen sulphide and venting the latter into the air, as is sometimes possible, even when the corrosion cost is taken into consideration. The more stabil sulphur compounds, including the thiophenes, are readily removed from straight run gasolines by concentrated sulphuric acid 98 to 99%, and sulphuric acid is as yet the cheapest desulphurising chemical that we have; it is easily handled and cheaply recovered. With cracked gasolines high sulphur content is rather exceptional, and the use of sulphuric acid at low temperatures, now practised in California, has greatly reduced the refining losses formerly incurred there with such gasolines. The point to be emphasized therefore with regard to research on this problem is the rather severe economic limitations on any chemical method of solving this problem. The first essential in any industrial research problem is to find out what "par" is with respect to cost. In the case of the sulphur problem the limiting cost is usually very low.

The Cracking of Rangoon Paraffin Wax with $AlCl_3$ at Temperatures below 330° C.*

By H. I. Waterman, Ph.D. (Member), and L. L. W. van Soest.

Rangoon paraffin wax (molecular weight, Rast method, 414; setting-point, Shukoff method, 57·7° C.), was used in this investigation.

The Apparatus used and the Method of Working.

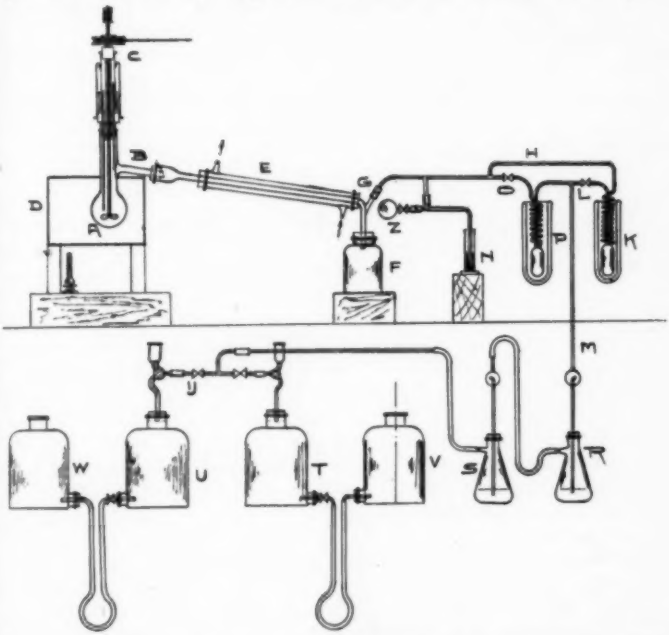
The paraffin wax was brought into the flask A (see diagram), which was heated by an asbestos airbox, and provided with a stirrer shut off by mercury. The vapours were conducted through the tube B to the water-cooled condenser E. The distillate was collected in the bottle F, the uncondensed gases passing *via* tube H to the vessel K, cooled with CO_2 and alcohol, and afterwards *via* cock L and tube M to the vessels R and S, which were filled up with dilute potassium hydroxide solution, and next to one of the bottles U and T. The vessel P, which was also cooled by solid CO_2 and alcohol, was used as a reserve vessel, in the event of vessel K being obstructed or filled up altogether, the cock L being closed and O opened. Thus it was still possible to condense low boiling gasoline. After each experiment the contents of the vessels P and K were evaporated at ordinary temperature, and the gases then developed added to the gases in the bottles U and T. The remaining light gasoline was added to the product already accumulated in F. Before the beginning of the experiment the apparatus was filled with CO_2, which during the experiment was absorbed in the vessels R and S. After each experiment the apparatus was still filled up with the gases formed during the last period. It was possible to take a sample of this gas in the evacuated ballon Z, and thus the sp. gr. of the remaining gas could be determined.

The gas in the bottles T and U was measured and also a simple gas analysis made. About 10 per cent. of $AlCl_3$ was added to the paraffin wax (300-800 gr.), carefully dried in advance.

The $AlCl_3$ was partly prepared from Al and HCl, and partly from trade products. Generally we worked with a vacuum of a few cm. of mercury. The small vessel N, filled with mercury,

* Paper received October 3, 1928.

functionated as a security and at the same time it served to control the vacuum in the apparatus. The heating was executed by gradually increasing the temperature till the first gasoline was collected in the vessel F, then the temperature was kept constant during the proceeding of the cracking-process. The temperature was increased when there was an important decrease in the gasoline production. This was repeated till at last the increase of temper-



ature was no more of any advantage and only paraffin wax was separated in the condenser E, but no gasoline was obtained. The production of gasoline finished because the $AlCl_3$ was apparently no more active and the temperature as such was not high enough to crack the remaining paraffin in flask A without the contribution of the $AlCl_3$.

What is Happening During the Experiment?

We observed already at low temperature, *e.g.*, 180° C. measured in the liquid, the beginning of the formation of gasoline drips at the end of the condenser. The mass in the flask was very soon coloured brown, and then darker, especially by the separation of

"carbon." As mentioned already the heating was increased as soon as the production of gasoline began to diminish. Finally we find the formation of a paraffin-deposit in the condenser tube, the temperature then, *e.g.* increasing to 300° C. Each experiment generally lasted about three hours. There was only a slight formation of HCl when the paraffin was quite dry.

In the gases we found a small percentage of unsaturated hydrocarbons. In addition to the paraffin, which was separated at the end of the experiments in the condenser there was also, in the cracking flask at the end of the experiment, a quantity of paraffin which could be separated from the formed "carbon" and the $AlCl_3$-residues by melting. This paraffin remaining in the cracking flask behaved as unchanged Rangoon-paraffin on a new experiment with the addition of fresh $AlCl_3$.[1]

Investigation of the Products Formed.

The gas.—As already mentioned we found a small percentage of unsaturated hydrocarbons. Hydrogen was not found in practically important quantities notwithstanding an accumulation method in which the hydrocarbons were condensed by cooling with liquid air. We determined the liter-weight of the gas. The gas which was present in the apparatus after each experiment had a liter-weight of 2·6. The average composition of the gas agrees with butane.

From the *gasoline* we determined the sp. gr., the refractive index (nD) and the bromine value (addition). The specific weight (20·4°) was between 0·65 and 0·68 for the gasoline boiling to 220°. The refractive index (nD^{20}) was between 1·381 and 1·397. The bromine value (addition-method of McIlhiney) was practically zero. As highest value we found 2. The gasoline had a low initial boiling-point (I.B.P. about 25°); more than 60 per cent. generally distilled below 100°.

Investigation of the Paraffin Wax Left in the Cracking Flask and of the Paraffin Wax Distilled into the Condenser-tube.

Both products were wholly saturated towards bromine. The bromine number practically was zero. The highest value which was found, was 1.

The setting point Shukoff method varied with the residue paraffin wax from 57·1 to 59·5° C. The highest setting point of 59·5° was obtained in that experiment at which the bromine value of the gasoline was about 2 and that of the residue paraffin wax 1.

[1] See also H. I. Waterman and J. N. J. Perquin, *Journ. Inst. Petr. Techn.*, 1927, **13** (62), 422-423.

In this experiment also the greatest quantity of paraffin was distilled into the condenser. Apparently after the action of the $AlCl_3$ the ordinary cracking caused by the increase of temperature was predominating.

We determined the molecular weight by the recently improved method of Rast.[2] The different residue paraffin waxes gave molecular weights between 362 and 434. The molecular weight of the paraffin samples from the condenser (setting point between 39·7 and 50·0° C. in different experiments) varied from 249 to 300.

The yields of gasoline were between 18 per cent. and 23 per cent. The residue paraffin wax varied from 50 to 62 per cent. of the raw material. In the experiment where we supposed that, after the period of activity of the $AlCl_3$, the ordinary temperature-cracking was predominating, the quantity of the residue paraffin was about 30 per cent. The percentage of the paraffin wax in the condenser was about 17 per cent., in the other experiments it varied from 2 to 5 per cent. The residue paraffin, behaving as ordinary Rangoon paraffin on the addition of fresh $AlCl_3$, the yields of gasoline are calculated on the quantity of the original paraffin extracted with the sum of the residue paraffin and the condenser-tube paraffin. The thus calculated net yields of gasoline were 34 per cent. as a minimum and 54 per cent. as a maximum. Only in a single experiment was the $AlCl_3$ more active. Under analogous circumstances the primary yield of gasoline was much higher than 23 per cent., namely, 31 per cent. In this experiment, even after heating to 405° C., the $AlCl_3$ was still active, and therefore the yield of gasoline might no doubt be still higher here, but there were other reasons which necessitated us to finish this experiment and the result was that the yield of gasoline calculated on unchanged paraffin was 48 per cent. and not higher than in other experiments.

These observations are chiefly in accordance with the investigations of A. Pictet and I. Lerczynska[3], who, in their experiments, added 10 per cent. by weight of $AlCl_3$ and who obtained, using Galician paraffin as a raw material, 35 per cent. of a gasoline boiling between 40° and 140° and 13 per cent. of a gasoline boiling between 140° and 180°. We suppose that the $AlCl_3$ in our experiments works in two manners. Primarily, it causes the cracking at a lower temperature. Therefore the decomposition will be less intensive than at higher temperature (cracking without $AlCl_3$). Secondarily, the unsaturated products eventually formed will be

[2] H. I. Waterman, J. N. J. Perquin and H. van Westen, *Journ. Inst. Petr. Techn.*, 1928, **14** (67), 318.
[3] *Bull. Soc. Chim.*, 1916, **19** (4), 326.

attacked by the $AlCl_3$ and the result is the formation of products wholly saturated.[4]

The action of the $AlCl_3$ is limited ; this is proved by the important quantity of residue paraffin. It seems that we have to deal here with unchanged or almost unchanged paraffin. It is very difficult to decide this, for it may be possible that, by a combined distillation process, which causes an increase of the molecular weight of the residue and a cracking which causes a lowering of the molecular weight, a condition apparently stationary is created. Therefore the paraffin separated in the condenser-tube may be caused by the distillation of the lower boiling paraffin of the Rangoon wax or by a mild cracking of this paraffin wax.

In the experiment where the $AlCl_3$ had ceased to be active and yet the heating was continued during rather a long time there could be expected a certain percentage of unsaturated products in the gasoline.

Delft, Laboratory of Chemical Engineering of the
Technical University.
September, 1928.

[4] W. A. Gruse, Petroleum and its Products, New York, 1928, pp. 62-63.

The Fundamental Factors of Liquid Phase Cracking.*

By Dr. A. N. Sachanen (Sachanov) and M. D. Tilitsheyew.

The results of cracking depend upon four fundamental factors: duration of the process, temperature, pressure, and the character of the oil product used. In order to get a deeper insight into the fundamental laws governing the phenomena of liquid phase cracking different petroleum fractions, with rather narrow distilling ranges have been used for cracking, as follows:—

1. Gasoline fraction (naphtha) 180–220° C.
2. Kerosine fraction 220–270° C.
3. Gas oil fraction 270–300° C.
4. Solar oil fraction 300–325° C.
5. Engine oil fraction 250–280° C. at 6mm. pressure.
6. Cracked kerosine fraction 220–270° C.
7. Cracked gas oil fraction 270–300° C.

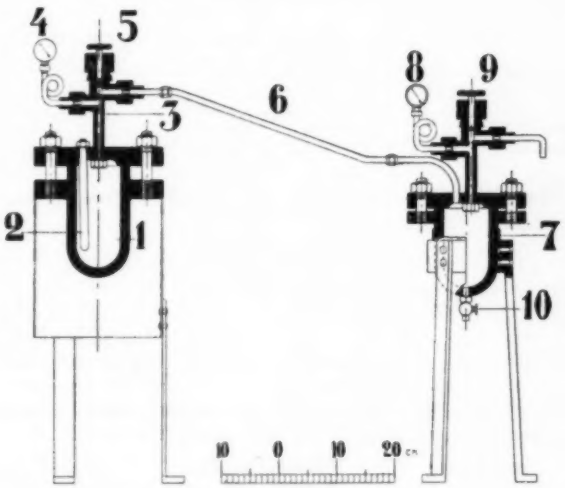


Fig. 1.

All the above-named fractions were obtained by fractional distillation of crude oils, chiefly from the Grosny fields. The cracking experiments were performed in the apparatus shown in Fig. 1, and the mode of operation has been described in an earlier

* Paper received July 17, 1928. Edited by Mr. R. Pitkethly.

article by us.[1] The results of these runs are given below. The yield of all the cracked products are calculated in per cent by weight.

Cracking of the Different Fractions.

Conditions.—Temperature 425° *C. Duration* 64 *min.*

1. *Gasoline.*—180°–220°. Sp. gr. 793. Final pressure 100 atmospheres.

Distillation.	Before Cracking. Yield %.	Sp. gr.	After Cracking. Yield %.	Sp. gr.
Gas and loss	—	—	5·1	—
Distillate to 180°	—	—	12·1	0·728
180–200	32·5	0·788	19·2	0·789
200–220	43·5	0·794	36·2	0·797
220–230	11·3	0·800	9·3	0·805
Residue	10·7	0·812	14·4	0·834

2. *Kerosine.*—220°–270°. Sp. gr. 0·810. Final pressure 85 atmospheres.

Distillation.	Before Cracking. Yield %.	Sp. gr.	After Cracking. Yield %.	Sp. gr.
Gas and loss	—	—	2·3	—
Distillate to 200°	—	—	14·9	0·728
200–220°	4·3	0·800	11·5	0·799
220–270°	84·7	0·809	56·3	0·818
Residue	6·8	0·830	12·8	0·861

3. *Gas Oil.*—270°–300°. Sp. gr. 0·834. Final pressure 70 atmospheres.

Distillation.	Before Cracking. Yield %.	Sp. gr.	After Cracking. Yield %.	Sp. gr.
Gas and loss	—	—	2·7	—
Distillate to 200°	—	—	15·8	0·731
200–270°	—	—	15·1	0·826
270–300°	63·9	0·833	30·7	0·842
Residue	35·6	0·839	31·3	0·871

4. *Solar Oil.*—300°–325°. Sp. gr. 0·859. Final pressure 72 atmospheres.

Distillation.	Before Cracking. Yield %.	Sp. gr.	After Cracking. Yield %.	Sp. gr.
Gas and loss	—	—	*16·7	—
Distillate to 200°	—	—	17·6	0·728
200–300°	—	—	24·4	0·845
300–325°	87·3	0·853	36·1	0·875
Residue	11·4	0·904	15·3	0·912

* High gas loss due to leakage—gas estimated at 4%.

[1] *The Refiner*, 1927, **84**, 6, No. 10.

5. *Engine Oil.*—250°–280° at 6mm. pressure. Sp. gr. 0·910. I.B.P. 248°. F.B.P. 290° at 6mm. pressure. Final pressure 72 atmospheres.

Pressure.	Distillation.	After Cracking. Yield %.	Sp. gr.
Atmosph.	Gas and loss ..	6·7	—
,, ...	Distillate to 200° ..	22·4	0·735
,, ...	200–300° ..	18·9	0·851
5 m.m.	145–200° ..	7·4	0·908
,, ...	200–250° ..	14·4	0·945
,, ...	250–285° ..	14·5	0·963
,, ...	285–346° ..	6·1	0·989
,, ...	Residue ..	4·0	—

6. *Cracked Kerosine.*—220°–270°. Final Pressure 85 atmospheres.

Distillation.	Before Cracking. Yield %.	Sp. gr.	After Cracking. Yield %.	Sp. gr.
Gas and loss	—	—	3·3	—
Distillate to 200°	—	—	15·3	0·733
200–220°	3·8	0·811	4·6	—
220–270°	85·4	0·826	53·2	0·833
Residue	9·4	—	21·3	0·890

7. *Cracked Gas Oil* 270–300°. Sp. gr. 0·846. Final pressure 61 atmospheres.

Distillation.	Before Cracking. Yield %.	Sp. gr.	After Cracking. Yield %.	Sp. gr.
Gas and loss	—	—	2·8	—
Distillate to 200°	—	—	12·5	0·744
200–270°	7·3	0·840	20·4	0·834
270–300°	80·0	0·843	40·0	0·850
Residue	12·5	0·856	22·6	0·892

From the above results some general deductions may be made. Cracking provides not only light products of decomposition, but also products of condensation, which are characterised by relatively high specific gravities.

The products of cracking usually consist of (1) gas, (2) gasoline, (3) kerosine, (4) gas oil, and (5) high boiling fractions. The formation of high boiling fractions is clearly seen in the above experiments. By fractional distillation in vacuo these synthetic high boiling fractions can be easily separated.

The original oil after cracking becomes a complicated mixture of the original and cracked fractions, and with the continuance of the process the quantity of cracked gasoline increases not only on account of the continued cracking of the original oil but is also due to the decomposition of cracked fractions heavier than cracked gasoline.

The velocity of cracking at a constant temperature gradually decreases with the duration of the process due to the diminishing

quantity and concentration of the original oil (and of the newly formed oils of decomposition heavier than cracked gasoline). Thus cracking the gas oil fraction at 425° for 30 minutes gives 8·4 per cent. of cracked gasoline, for one hour 15·8, and for three hours 24·6 per cent. In the first stages of the process there is a direct ratio between the quantity of the cracked gasoline formed and time of process. This is clearly illustrated by experiments on cracking of a heavy Russian crude oil.

These results confirm previously obtained data[1] and show that cracking begins immediately after the necessary temperature conditions have been reached, and that there is no " induction period " during which the process of gasoline formation does not take place, as is assumed by some authors.[2]

The velocity of cracking under the same conditions depends very much on the nature of the oil to be cracked. The velocity is lowest for the lightest fractions, and gradually increases for heavier fractions ; for instance, gasoline fraction 180–220° gave 12 per cent., whilst engine oil gave 22 per cent. of cracked gasoline under the same conditions.

Cracked oils decompose at a slower rate than straight run oils. In this respect the experiments are in agreement with those of Leslie and Potthoff, who found that thermalised gas oil requires twice the time necessary to crack straight run gas oil.

The velocity of cracking depends very much on temperature, doubling for every 10 degrees Centigrade. This fact makes it possible to calculate the velocity of cracking at different temperatures, if the velocity is known at a certain temperature, as the velocity of cracking of all high boiling oil fractions is practically the same when other conditions are constant. The time required to form 10 per cent. 20 per cent. and 30 per cent. of cracked gasoline at different temperatures has been studied. The results of these experiments are of importance, as it may be seen that if low boiling products such as kerosine or gas oil are cracked the time factor must be increased up to $1\frac{1}{2}$ times. A temperature of 450 to 475° C. appears to be the optimum for liquid phase cracking, as this temperature secures a high velocity of decomposition, but further raising of the temperature causes a rapid formation of coke and a high pressure. Cross and Dubbs use temperatures of 440 to 490° C.

The velocity of cracking does not depend on pressure, as experiments prove that the yield of gasoline and kerosine remains the same for pressures of 10, 20, 30 and 40 atmospheres when the temperature and time of reaction are constant. The application

[2] *Neftianoie Chozíaistvo* (russ.), 1928, N3, 328-353.

of high pressure, however, produces the best conditions for heat transfer and absence of local overheating with economy of fuel.[3]

It has been already stated that condensation is demonstrated by the increased specific gravity of the heavier cracked fractions. Comparison of the specific gravities before and after cracking of the fractions investigated show that the specific gravity of gasoline increased from 0·794 to 0·797, the kerosine from 0·809 to 0·818, the gas oil from 0·833 to 0·842, and the engine oil from 0·910 to 0·963. Condensation appears to take place readily in the heavier fractions but is almost absent in the lighter fractions. This effect is also demonstrated by cracking a Baku mazut and distilling the product up to 300° C. The specific gravity of the residues above this temperature after cracking at constant temperature but for different periods rises steadily with increase of time. When cracked at a temperature of 426° for 22 minutes the gravity of the residue above 300° rises from 0·890 to 0·903, in 32 minutes to 0·906, in 62 minutes to 0·923, in 92 minutes to 0·932. This rise in specific gravity is not due exclusively to concentration of high boiling compounds contained in the original oil. The increase in specific gravity is not always accompanied by formation of high boiling substances, as lower boiling products of decomposition often possess a higher specific gravity than the original oil, as is noticeable in the cracking of engine oil.

The final stage of condensation is the formation of coke, and the connection between condensation and coke formation may be seen in the cracking of spindle oil or engine oil. When engine oil is cracked at 452° C. for approximately 30, 60 and 90 minutes the yields of gasoline are practically 10, 20 and 30 per cent. the kerosine 13, 17·5 and 20 per cent., the specific gravity of the residues are 0·964, 1·004, 1·080, whilst the yields of coke are nil—0·15 and 1·35 per cent. respectively. There is a definite connection between the formation of high gravity residue and coke formation. The former is the material from which coke is formed. Thus, in the first stages of cracking oil distillates coke formation does not take place, and begins only when products of condensation in the shape of high specific gravity oils have been formed. Distillates of the same specific gravity cause less coke formation than residues or heavy crude oils. This is explained by the presence in the latter of high specific gravity oils, and also of resins and asphaltenes which form coke very easily.

The velocity of coke formation increases with increasing time of cracking. This is in striking contrast to the phenomena of decomposition which proceed with high velocity at first but gradually

[3] Auld and Dunstan, *Ind. Eng. Chem.*, 1926, **18**, 803.

become slower with prolongation of the cracking. While the products of decomposition decrease with increasing time of cracking, the quantity and concentration of the products of condensation gradually increase and the velocity of coke formation also gradually increases.

Too long a period of cracking and production of the highest yield of cracked gasoline in one run is disadvantageous, because after a certain time the velocity of gasoline formation is very slow ; and, on the other hand, the velocity of coke formation becomes very high. Therefore, it is economically more advantageous to stop cracking in the first cycle when coke formation begins and produce more gasoline by re-cycling those fractions which do not form great quantities of coke during cracking. Temperature has a considerable influence on coke formation, and experiments carried out on certain crude oils and residues show that the velocity of coke formation increases sixfold for every 25° C. It is useless to lower the temperature in order to lessen the coke formation, as a certain yield of gasoline always corresponds to a definite yield of coke. Pressure, has little if any influence on coke formation.

For the purpose of studying the effects of repeated cracking, or re-cycling, a light gas oil, specific gravity 0·833 with 86 per cent. boiling between 200° and 350° C. was used. The first run at 450° C. for thirty minutes yielded :—

4·4 per cent. gas and loss ;

17·5 per cent. fraction below 200° s.g. 0·730 ;

76·3 per cent. residue above 200° s.g. 0·855.

The cracked gases amounted to 44 litres per kilogram of cracked gasoline. The residue above 200° was again cracked, and the residue above 200° separated and cracked for the third and fourth time.

In the last case the cracked gases amounted to 377 litres per kilogram of gasoline, and a considerable amount of coke was formed (13 per cent.), while no coke was formed in the first three runs. After the fourth run the cracked kerosine may be further cracked to yield 20 to 25 per cent. of gasoline, but the residue above 300° undergoes condensation to such a degree that a material yield of gasoline cannot be obtained.

The results of the four successive experiments giving yields in per cent. by weight of the original gas oil are as follows :—

	Gasoline.	Residue.	Gas.	Coke.	Sp. gr. of residue.
1 ..	17·5	81·8	0·7	0·0	0·855
2 ..	39·7	55·6	4·7	0·0	0·893
3 ..	49·0	43·6	7·4	0·0	0·920
4 ..	55·2	33·3	8·8	2·7	0·975

After repeated runs the gasoline yield approaches a certain limit, which is about 60 per cent. with moderate coke formation, or 65 per cent. with considerable coke.

These results are in agreement with American technical data as obtained from Cross and Dubbs' processes.[4] As may be seen from the above data, the lower velocity of decomposition of cracked oil becomes apparent when the first and fourth runs are compared. The duration of the fourth run was three times that of the first run, yet the yield of gasoline is nearly the same. The specific gravity of the cracked gasoline rises from 0·730 to 0·770, indicating the progressive formation of aromatic compounds. The increase of cracked gas in each run is noticeable.

It is obvious that there is a limit to the technical application of repeated cracking beyond which the process is uneconomical.

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[4] Leslie, *Motor Fuels*, 1922, 322. Cross, "Handbook of Petroleum," 1924, 314.

Launching a 5,000 ft. Submarine Oil-Loading Line.*

G. C. Maclaran (Member).

As the launching of submarine oil loading lines is a somewhat uncommon proceeding, this paper has been written in the hope that it may be of some interest both to those who have to deal with the problems which crop up on an oilfield and to others whose interest in oil matters is from a less practical point of view.

The line concerned was launched from the property of the Lobitos Oilfields, Ltd., in Peru, to whom thanks are due for permission to write this paper.

A new sea loading line had become essential in order to ensure a sufficiently high loading rate for present day and future tanker requirements. It was further necessary to carry out repairs on the existing line, which had been giving trouble and which was not considered to be in a dependable condition.

The procedure and arrangements finally adopted were evolved to meet local requirements, and having proved successful are described in detail.

The distance from the Mole head to the tanker moorings is 4,500 ft., and as the line had to be launched from the shore and allowance made for drift, etc., it was seen that 5,000 ft. of pipe would have to be prepared for launching.

The ground in the vicinity of the Mole did not give much encouragement to the undertaking, and it was at once apparent that it would be impossible to connect up and pull out the line in one length of 5,000 ft. long. Low hills start rising sharply a short distance inland from the shore and just over 1,000 ft. was the most that could be hoped for in the way of a reasonable runway for launching purposes.

Trouble with the old line was being experienced on a section of about 400 yards from the shore out to sea. The line appeared to have deteriorated more rapidly on this section than elsewhere. It was therefore decided to bring the new line up from the sea bottom at the end of the Mole and to connect up with the pumps on shore by laying the line along the Mole and so avoid laying any pipe through the surf.

* Paper received 8th August, 1928.

PHOTOGRAPH NO. 1. THE FIVE LENGTHS OF PIPELINE READY FOR LAUNCHING.

PHOTOGRAPH NO. 2. THE TEMPORARY PIER AND THE SEA END OF THE PIPE-LINE WITH FLANGE AND CARRIAGE IN POSITION.

UNIV. OF MICH.

PHOTOGRAPH NO. 3. THE SEA END OF THE LINE WITH HOLDING CLAMPS IN POSITION.

PHOTOGRAPH NO. 4. THE END OF THE PIPELINE ON BOARD THE RAFT WHICH CAN BE SEEN TO THE LEFT OF THE MOLE HEAD.

The pipe selected for the line was 9 in. inserted joint casing, the particulars of which are as follows :—

External diameter	9·09″
Internal diameter	8·5″
Thickness	0·295″
Number of threads per inch	10·
Length of threaded portion	5·12″
Weight of pipe per ft.	27·606 lb.
Weight of sea water displaced per foot	28·871 lb.
Buoyancy of empty pipe per foot	1·265 lb.

The pipe is ordinary stock casing as used in the wells on the field and had distinct advantages over collar pipe in this instance. The length of the threaded portion of the inserted joint casing is 5·118 in. as against 3·5 in. in ordinary collar line pipe. This in itself is a big advantage, giving a stronger joint under either direct pull or side strains. It can readily be realized that it is impossible to avoid drift and side strains in handling a length of 5,000 ft. of pipe floating in the sea. The absence of collars also gives the pipe a smooth joint which will pass freely over rollers and not drag or catch in the sand. It will be noted that the empty pipe was buoyant to the extent of 1·265 lb. per ft.

The mode of procedure decided on was as follows :—

The line was to be connected up on shore in five lengths of approximately 1,000 ft. each on a runway giving a straight pull in a direct line with the moorings.

As each length was pulled out another length was to be coupled to it until the whole 5,000 ft. had been pulled out.

The ends of the line were to be plugged in order to take advantage of the buoyancy of the pipe.

The sea end of the line was to be sunk as soon as it arrived over the desired position at the moorings.

The shore end was to be floated over against the Mole—cut at the required point and sunk in position with the flange fitted ready to take the bends to bring the line up to the required level on the Mole.

Once actual pulling out started every effort was to be made to carry through the launching and sinking with as little delay as possible in order to reduce the risks of breakage with a long length of pipe floating in the sea.

Shore Arrangements.—The five lengths of pipe were coupled up parallel to one another with the first length to be pulled out resting on cast iron rollers spaced approximately 25 ft. apart. The four remaining lines were arranged on timber set at an angle to facilitate levering down on to the rollers when required. Photograph No. 1 shows the arrangement. A plentiful supply of railway sleepers

available at the time proved very useful for the purpose. All five lines were tested under hydraulic pressure.

Extra heavy forged flanges were finally decided on for coupling up the lengths of line, and these were made sufficiently deep to utilize the full length of the threaded portion of the pipe. This ensured that there would be no weakness at the flanged joints. Flanged joints were adopted in preference to the alternative welded joint as being quicker to make and more reliable.

The flanges for the sea ends of the five lines were fitted at once. Those for the inshore ends of the lines were prepared with nipples ready for screwing into each line after it had been pulled out. This was done as the flanges would not have passed freely over the rollers. It was also necessary to have the ends of the lines free for screwing in the eye nipple for attaching the breaking line which is described later.

At the beach a light temporary pier was constructed to carry 250 ft. of portable railway track. The purpose of this was to provide a track for the light timber carriage made to carry the flanges, after coupling up, across the beach. The track was carried well out into the surf. The photograph No. 2 shows the pier and the sea end of the pipe line with the carriage just behind the flange on the end of the pipe.

In order to maintain complete control over the shore end of the line while pulling out, and to ensure against the possibility of over pulling, braking gear was provided. This consisted of a bull-wheel set up and securely anchored in a convenient position near the shore. The bull-wheel was an ordinary drilling bull-wheel with brakes fitted on both wheels. A snatch block was attached to a post securely anchored at the extreme in-shore end of the runway. A wire line was passed from the bull-wheel through the snatch block and attached to the end of each length of line being pulled out by means of the eye nipple and shackle. With this arrangement the line was under complete control and could be stopped at any time within a foot of the required point.

Photograph No. 3 shows the clamps used for clamping the inshore end of the pipe already pulled out to sea. The clamps are shown in position on the first length of pipe before pulling out started. The clamps were put on before the braking line was detached, and served to hold the pipe securely until the next length of pipe had been coupled to it. The braking line was then attached to the inshore end of the length just coupled up before the clamps were removed.

A control platform was erected near the beach giving an unobstructed view of all operations, and a steam whistle and flag

staff were provided for signalling and controlling pulling operations at sea.

Sea Arrangements.—In order to maintain the line as straight as possible while pulling out, it was decided to pull on an anchor placed beyond and in a straight line over the required final position of the end of the pipe-line at the moorings.

For the actual pulling a balsa log raft was made up and fitted with a bull-wheel driven by a Fordson tractor through a counter shaft and chain reduction gearing as shown in Fig. 1. The bull-wheel was provided with 6000 ft. of old wire drilling line.

The end of the 6000 ft. wire line was to be attached to the anchor, and the line paid out until the balsa raft was sufficiently close in

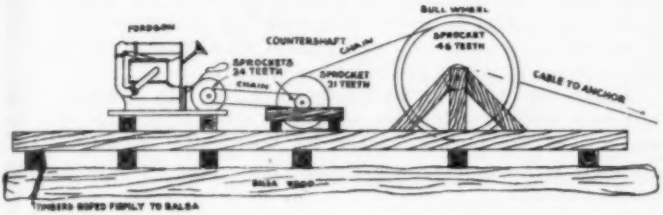

FIG. 1.

PULLING BALSA ON WHICH PIPE-END WAS CLAMPED.

shore to take on board the sea end of the first length of pipe. Pulling out was to be done by the bull-wheel and Fordson winch outfit winding in the line to the anchor, and so drawing the raft with the sea end of the pipe-line out with it. In the event of the load proving too much for the Fordson, launches were to assist.

The sea end of the line was fitted with its permanent flange. To this was bolted a temporary flange with a short 4 in. nipple and 4 in. gate valve, the object of this being to control the sinking of the line when in position by regulating the flow of water into the pipe. A similar flange with nipple and valve was fitted to the extreme inshore end of the line. The latter was to be used to control the sinking of the inshore end of the line after the sea end had been sunk in position by releasing the air.

Eight empty 50 gallon oil drums were provided. Two of these drums were to be roped to each flanged joint as it left the rails at the end of the pier in order to provide the additional buoyancy required to float the extra weight of the flanges.

The prevailing winds and current are from the south, and means had to be provided to prevent the pipe-line from being carried

too far out of line. For this purpose five balsa log rafts were anchored at equal distances apart to the south of the line of the pull. A rope from each of these rafts was to be passed loosely round the pipe-line as it was hauled out and so assist in keeping it in position.

A flag staff was provided on the winch raft for signalling to the control platform on shore.

Three launches and a small motor vessel were available to assist as required.

Launching the Line.—The possibility of pulling the whole line out and getting it sunk in position in one day had been considered and abandoned as not ensuring a sufficient margin of time. As there would be less risk with a short length of the pipeline left over night floating in the sea than with four or five thousand feet, it was decided to pull out one length in the afternoon and to complete the launching on the following day.

A start was made in the afternoon of the 11th January. The raft with winch was brought as close in shore as possible, and the sea end of the pipe-line taken on board and securely lashed. Photograph No. 4 was taken at this stage. The pipe-line can just be seen awash.

The holding clamps were removed and the pulling out of the first length commenced at 4 p.m. A controlling strain was maintained with the braking gear and pulling out continued until the eye nipple with braking line attached arrived opposite the flange of the next length of line to be coupled up. The steam whistle at the control platform was then used to stop the winch on the raft and the brakes were applied on shore. The holding clamps were next put on, the braking line disconnected and the eye nipple unscrewed and replaced by the nipple with flange. Gangs with levers were meanwhile employed in levering the next length of pipe-line down on to the rollers. The eye nipple was removed to the inshore end and screwed into the pipe and the braking line attached. To bring the flanges together for bolting up, light two and three ply tackle blocks were used to ease the line down the rollers. As the line only required to be pulled down the rollers a foot or so no difficulty was experienced in bringing the two flanges to register and making the joint. The truck was next placed under the pipe just behind the flanged joint, and the line left over-night with the first length pulled out to sea.

Pulling out was resumed at daybreak the following morning. The holding clamps were removed and the line was pulled out until the truck carrying the flanges reached the end of the rails and fell off into the sea. A momentary stoppage at this point allowed

sufficient time for the roping on of the empty cylinders at the flanges.

The launching of the remaining lengths of the line was carried out in a similar manner and without hitch of any kind. The inshore end of the line had left the beach and been taken on board a balsa raft some 200 ft. before the sea end arrived in position. As soon as the sea end of the line reached the desired spot at the moorings the line was dropped overboard with the 4 in. valve open. As the valve at the inshore end was still shut this allowed of the sinking of the greater part of the sea end, while the inshore end of the line remained buoyant owing to the air trapped in the pipe. The shore-end of the line was floated over against the side of the Mole and secured, and the line now being in position the valve was opened and the remainder of the line with the exception of the portion lashed to the Mole sunk. The line was next cut and a nipple and flange fitted at the required point under the Mole before the end of the line was finally lowered to the sea bottom. The flanged bends, to bring the line up to the required level on the Mole, were connected up at a later date with the aid of a diver.

The launching of the line had been completed by 3 p.m. on January 12th. The total working time from the commencement of pulling operations until the line was brought in against the Mole and finally sunk amounted to thirteen hours. The arrangements made by Mr. J. S. Massie, the Company's Marine Superintendent, were largely responsible for the facility with which the launching was carried out.

The International Committee on the Nomenclature of Materials and Processes Used in the Construction of Roads, and the Standardization of Testing Methods for Tars, Bitumens and Asphalts.

By PERCY E. SPIELMANN, Ph.D., B.Sc. (Member).

Two years ago (see this Journal, 1926, 12, 655) the International Roads Congress, held at Milan, called into being an International Committee to bring into orderly understanding the meaning of the words used in connection with road-making. In addition, it was to establish the tests to be applied to the cementitious materials employed in road-construction and their relative importance amongst themselves.

Two meetings took place in Paris, with M. Lorieux as Chairman and M. P. Le Gavrian as General Secretary, at the headquarters of the Permanent International Association of Road Congresses; the first was held at the end of June, 1927, and the second at the end of June, 1928.

The countries represented on the Committee were the following:—Belgium (Van Volsom, Ingénieur en chef Directeur des Ponts et Chaussées, Liége), Denmark together with Norway and Sweden (C. J. Brodersen, Directeur de l'Administration technique de la Municipalité de Frederiksberg), France (P. Le Gavrian, Inspecteur Général des Ponts et Chaussées, Paris), Great Britain (Dr. Percy E. Spielmann), Holland (Prof. F. J. Nellensteyn), Italy (Ing. Italo Vandone, Direttore dell' Instituto sperimentale stradale del Touring-club Italiano, Milan), Spain (Conde de Casa Rul, Professeur à l'Ecole des Ponts et Chaussées, Madrid), Switzerland (Dr. Schläpfer, Professeur à l'Ecole Polytechnique Fédérale, Zürich. Also Director of the Institute for Testing Materials).

The American representative, E. F. Kelley, Bureau of Public Roads, Dept. of Agriculture, Washington, did not attend.

The results attained were definite and valuable and international agreement was reached, except in one case ("asphalt") where, at second best, differences of significance were clearly established.

The business of the meeting was conducted in an excellent spirit of cordiality, and international friendship has been improved by the very exercising of it.

Nomenclature.

The chief conclusion—in fact the origin for the necessity for an international understanding—was connected with the words "asphalt" and "bitumen." They have always been used vaguely within the various countries and contradictorily as between them. The removal of this uncertainty became, therefore, the most important problem, and with its resolution were included the terms "tar" and "pitch."

A considerable number of important discussions took place in this country to determine the British attitude, followed by a close and critical one in Paris—when France made a concession of considerable national importance in connection with the word "asphalt." The final decisions were the following :—

Bitumen.—"Mixtures of natural and pyrogenous hydrocarbons and of their non-metallic derivatives, which may be gaseous, liquid, viscous or solid, but must be completely soluble in carbon disulphide."

This is the American definition, pure and simple, and obviously has very wide implications.

Asphaltic Bitumen.—"Natural or naturally occurring bitumen or bitumen prepared from natural hydrocarbons or from derivatives of natural hydrocarbons by distillation or oxydation or cracking ; solid or viscous, containing a low percentage of volatile products ; possessing characteristic agglomerating properties, and substantially soluble in carbon disulphide."

The logic of this new term is that it comprises that type of material from among all the bitumens which have the agglomerating properties necessary for the manufacture of asphalt.

Asphalt.—"Natural or mechanical mixtures in which the asphaltic bitumen is associated with inert mineral matter."

There is no implied limit as to size of grain of the mineral matter, nor as to the proportion of this to the cementitious material.

Asphaltite.—"Mixtures of asphaltic bitumen with finely divided organic matter insoluble in carbon disulphide."

This definition was adopted in order to include Gilsonite, Albertite and the like, which were excluded by the definition for Asphaltic Bitumen.

Tar.—"A bituminous product, generally viscous, of the condensation of the volatile compounds evolved during the destructive distillation of the hydrocarbon substances in coal, schists, lignite, peat, vegetable matter, etc."

Pitch.—"The residue resulting from the distillation of tar."

It will be seen that only the definition for "Bitumen" shows any important change from what has always been understood in this

country ; the rest are matters of detail. It is to be hoped, therefore, that the new definitions will find easy general acceptance : they have already been adopted by those who are most nearly affected by them.

Another important section of this subject is the publication of an International Lexicon of Road Terms, which is in active preparation. Each nation has undertaken a specific section : Great Britain and France have collaborated over the Asphaltic Bitumen and Tar Section. It is planned to appear in English, French, Italian, Spanish, Danish and German ; the Paris office will prepare the French edition, which will be sent to the various countries for the production of their particular volumes. There will probably be another meeting in Paris for the consideration of the final draft.

Tests.

The general scheme adopted, for the tests to be applied to the bituminous materials used in road-making, is the following, which is divided into essential and useful tests.

A.—TAR.

I. Essential Tests.

Content of Water.

Object.—Determination of the percentage of water.

Method.—Mixing of toluene or xylene with the tar ; heating and collecting the water distilled over in a graduated and cooled vessel.

Consistency.

Object.—Determination of the resistance shown by the materia to penetration by a given body.

Method.—" Hutchinson " instrument for sticky tars. " E. P. C." Consistometre for fluid tars when the Hutchinson instrument shows no result that can be recorded.

The test must always be carried out at a temperature of 25° C.

Note.—The Committee draws the attention of laboratories to the importance of studying the two apparatuses in such a manner as to unite the readings supplied by the E. P. C. consistometre with those shown by the Hutchinson instrument, under the same conditions.

Free Carbon.

Object and Method.—Determination of the insoluble residue obtained by treating the tar with carbon disulphide or with xylene, chloroform or benzine, making allowance for the mineral matters contained in this residue.

Distillation Tests.

Objects.—Separation, within the limits of pre-determined temperatures, of the constituents of the material.

The limits of temperature are as follow :—(*a*) Below 170° C. ; (*b*) from 170° to 230° C. ; (*c*) from 230° to 270° C. ; (*d*) from 270° to 350° C.

The residue from the distillation is pitch.

The rate of distillation must be such that the quantity of distillate does not exceed 5 c.c. per minute and is not less than 2 drops per second.

II. Useful Tests.

Density.

Object.—Determination of the proportion of the masses of equal volumes of material and water.

Method.—It does not seem necessary to recommend any particular method, the processes currently employed in laboratories being sufficiently exact.

The temperature is fixed at 25° C.

The results may be expressed to two decimal places.

Acid Oils.

Object.—Determination of the substances absorbable by soda or the proportion of phenols contained in the tar.

Method.—Collect the product of the distillation of the tar between 170° and 270° C. Add soda solution. After shaking and settling the increase in the volume of the soda solution corresponds to 1 per cent. of phenol per cubic centimetre.

Mixtures Containing Naphthalene.

Object.—Determination of the percentage present.

Method.—A precise and practical method has not yet been devised (but will be studied). For an approximate determining, crystallisation shall be employed.

B.—PITCH, BITUMEN AND ASPHALTIC BITUMEN.

I. Essential Tests.

Penetration.

Object.—Determination of resistance shown by the material to penetration by a determined body.

Method.—The use of a penetrometer of which the characteristics are the same as those defined in the standard method adopted by the A.S.T.M.

Note.—This test should be carried out at a temperature of 25° C.

Softening Point.

Object.—Determination of the pasty state of the material.

Method.—The ball and ring apparatus, adopted by the A.S.T.M.

Loss on Heating.

Object.—Determination of the percentage of volatile matter.

Method.—Method adopted by the A.S.T.M.

Solubility in Carbon Disulphide.

Object.—Determination of the percentage of constituents soluble in carbon disulphide.

Method.—Either the filtration method or the centrifugal method may be used.

Ductility.

Object.—Determination of the ability of a material to stretch without breaking.

Method.—A simple and precise apparatus showing constant results does not exist. (To be studied.)

II. Useful Tests.

Density.

Object.—Determination of the proportion of masses of equal volumes of material and water.

Method.—It does not seem necessary to recommend any particular method, the processes currently employed in laboratories being sufficiently exact.

The temperature is fixed at 25° C.

The results may be expressed to two decimal places.

Penetration at Low Temperature.

Object.—Determination of resistance shown by the material to penetration by a determined body.

Method.—The use of a penetrometer of which the characteristics are the same as those defined in the standard method adopted by the A.S.T.M.

The test should be carried out at temperatures of 0° C. and −10° C.

Flash-point.

Object.—Determination of the lowest temperature at which, under normal pressure, a material gives off, under specified conditions, such a quantity of combustible vapours that, mixed with air, they momentarily ignite on contact with a flame.

Method.—The open test is recommended.

Free Carbon and Ash.

Object.—Determination of free carbon and ash.

Method.—The insoluble residue left after treating the material with pure carbon disulphide shall be used.

Solubility in Sulphuric Ether.

Object.—Determination of the soluble constituents in sulphuric ether.

Method.—The usual method.

C.—EMULSIONS.

I. Essential Tests.

Content of Water.

Object.—Determination of the percentage of water.

Method.—Mix the emulsion with toluene or xylene; heat and collect the water distilled over in a cold, graduated vessel.

Separation of Water and Bitumen.

Object.—Determination of the percentage of bitumen.

II. Tests which Merit Further Study and Discussion, with a view to Ultimate Standardization.

Plasticity Test.—The test suggested by M. Vandone* on asphaltic mortar or compressed asphalt should be specially studied with a view to testing bituminous road surfacings.

Adhesion Test.

Cohesion Test.

Test of Resistance to Atmospheric Agents.

Oxydation Test.

Study of Testing Methods which may give satisfactory results for ascertaining the quality of the stabilizers of emulsions.

Classification of Road Surfaces.

These are of no immediate importance to this Institution.

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* Details are not yet available.

REVIEWS.

PETROLEUM AND ITS PRODUCTS. A Chemical Discussion of the Properties, Refining and Utilization of Petroleum. By William A. Gruse, Ph.D. Published by McGraw-Hill Publishing Co., Ltd.

The author is a well known investigator on the chemistry of petroleum and many of his researches from the Laboratory of the Mellon Institute, Pittsburgh, are well known to members of this Institution.

It is impossible to avoid comparing Dr. Gruse's monograph with that of Gurvitsch and to some considerable extent the two works are complementary; Gruse viewing the subject from a western and Gurvitsch from an eastern standpoint.

The book under review is primarily concerned with the chemical aspect of mineral oil and the refining thereof and falls into three main sections.

The first ninety pages deal with the composition, classification and description of important types of petroleum followed by a disquisition on the chemistry of the hydrocarbon components, the oxygenated compounds, the resinous compounds, the thio derivatives and the nitrogenous bodies present in mineral oil. A short account is given of the chief group reactions of the raw material. The physical properties are dealt with briefly and this section ends with a chapter on the origin of petroleum in which attention is drawn to the interesting review of various organic theories given by Clark (*Journ. Inst. Petr. Techn.*, 1926, vol. 12, p. 257).

The middle section of Dr. Gruse's work is concerned with refining, and discusses the various processes of distillation, chemical treatment, adsorption and cracking from the point of view of the fundamental chemistry underlying the various reactions. If one could make a criticism here, it would be that not enough space is accorded to newer methods. It would have been advisable, for example, in chapter six to curtail the methods described and to have given much more space to modern pipe-still and bubble tower equipment and theory.

The last section contains a series of chapters that are concerned with the general technical fractions of petroleum, their properties and application.

One is again in this section rather apt to compare Dr. Gruse's work with that of Gurvitsch. Gruse has attempted to give a comprehensive picture of the whole treatment of mineral oil as the chemist sees it. Gurvitsch on the contrary has discussed in greater detail those parts of the chemical technology of mineral oil that particularly interest him.

The book is admirably printed and got up and is a credit both to the author and his publishers. A. E. DUNSTAN.

PETROLEUM-BOEK. [*Publications of the Dutch daily paper, "De Telegraaf."*] In Dutch. 389 pages octavo, with index.

This book, as stated in the Preface, written by the financial editor of "De Telegraaf," consists of different articles on the Petroleum industry and Petroleum policy published during more than a year past in that paper. The materials have been re-edited and brought up-to-date. The editor's object has been to form a book dealing with the varied problems arising both as regards the industry itself, and its political side.

The book itself, consisting of separate articles, deals very largely with the financial aspects of Petroleum, as arising from its production and utilisation all over the world. Commencing with the Royal Shell group, it covers all

the other well-known oil-producing companies. The Anglo-Persian Oil Co. is represented by an interesting and concise account of its origin and developments. Many details are also given in regard to a quantity of independent companies, such as the "Texas Oil Corporation," "Gulf Oil Corporation," the "City Services Co.," "the Marland Oil Co.," "the Sinclair Consolidated Oil Corporation," etc. The Standard Oil group naturally receives special attention. The second half concerns itself with Petroleum from the International standpoint: its over-production problem, and the efforts to control the output, and the difficulties connected therewith. Finally, a very useful set of statistics closes the volume. There are sundry portraits of the directors of well-known companies, attached to the descriptions of the same. As a book to read it suffers from its form—*e.g.*, the detached nature of the information; but as a book for reference it should prove of great value.

J. E. Marshall Hall.

BOOKS RECEIVED.

The Coalfields of Scotland. The Carbonisation of "Kinneil Gas" Coal. Dept. of Scientific and Industrial Research. London, H.M. Stationery Office, 1928. Pp. 35. 1s. 6d. net.

The present report is the eleventh of the series on the Physical and Chemical Survey of the National Coal Resources, and deals with the product of the Six Foot seam worked in the Kinneil Colliery, Linlithgowshire. In the low-temperature carbonisation tests, the coal carbonised at 625° C., yielding 14 cwt. of smokeless fuel per ton of coal. The yield per ton of other products were:—Tar, 19.5 gals.; liquor, 64 gals.; ammonium sulphate, 17.4 lb.; and gas, 8,680 cu. ft.; from which 1.5 gals. of light spirit were obtained.

Report of Fuel Research Board for the period ended March 31, 1928. Dept. of Scientific and Industrial Research. London, H.M. Stationery Office, 1928. Pp. 70. 1s. 3d. net.

This report contains the Report of the Director of Fuel Research for the year ended March 31, 1928, and describes in detail the operations carried out by the Board. The various sections deal with Coal Resources, the Gas Industry, Low-Temperature Carbonisation, Coke, Briquetting, Coal Purification, Hydrogenation of Coal, Internal Combustion Engines, Domestic Heating, Power Alcohol, and other miscellaneous subjects, and should form a valuable source of information.